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**THE RHEOLOGY OF COATINGS
IN APPLICATION
AND DRYING**

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DISSERTATION**



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IN APPLICATION AND DRYING

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The rheological changes during the drying period are analyzed from estimations of the changes in solvent balance as the drying proceeds and subsequently the changes in viscosity and solubility power of the remaining solvent. The theory predicting the evaporation of water from coating products and hence evaluate viscosity changes with evaporation in aqueous coatings.

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Foreword

This study is based on experimental results from projects for the Danish Technological Council and for the major part the Swedish Board for Technical Development, carried out at the Scandinavian Paint and Printing Ink Research Institute in the period 1974-78.

While the intentions of the projects have been to support industry in their technical development on certain subject areas, the core of this study has become the elucidation of the physical patterns controlling the application process and the development of methods characterizing significant properties with respect to this process. To achieve this a certain amount of existing information as well as knowledge from more basic sources and entirely different applied fields have been drawn upon. The practical work done in this study has become fragments in the patterns, where other sources have failed to provide the necessary information. Due to the nature of the projects, the articles and reports that this study refers to may be found more in-depth explanatory and thus more lengthy than if the scope was purely scientific.

Professor A. Björkman of the Technical University of Denmark and Professor B. Törnell of the Technical University of Lund have carried out the formalia of this rather unusual licentiate study. Assoc. professor P. Scheel Larsen of the Department of Fluid Mechanics has been very helpful in clarifying the physics of the evaporation problems. H.K. Raaschou Nielsen, formerly director of the Scandinavian Institute, is responsible for my initial involvement in this problem area and, by never failing enthusiasm and energy and his life-long experience in coatings and daily colleagues, especially Birthe Thorsbro, Ib Rasmussen, Birte Høgh Andersen, and Klaus Lampe have taken care, that the project have become related to practical coatings problems by their patience in answering a countless number of questions from a non-chemist with no coatings back-ground. Also my direct superior Ago Saarnak has been very patient in this respect. My director since 1975, dr. C.M. Hansen, has also had an impact on this study by his special ways and background.

Copenhagen., June 6th, 1980.

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This study is based on the following articles and reports:

- A Kornum, L.O. and Raaschou Nielsen, H.K., Surface Defects in Drying Paint Films, (accepted for publication in Progress in Organic Coatings).
- B Kornum, L.O., Rheological Characterization of Coatings with Regard to Application and Film Formation, Rheol. Acta 18 (1979):1.
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- D Kornum, L.O. and Lampe, K., Appliceringsteknikker - Højtryks-sprøjtning, Påføringsegenskaber for nogle vandfortyndbare malinge og nogle malinge med højt tørstofindhold, Teknisk Rapport T 15-77 M, Nordisk Forskningsinstitut for Maling og Trykfarver, Oktober 1977.
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Abstract

The flow problems related to the coatings application process have been analyzed from a physical point of view. The bulk rheology related to the application process have been evaluated from fundamental rheology. On this basis a relevant rheological characterization of the processing qualities has been proposed and practicable means of performing the measurements have been developed and access has been made to apply various rheological models to the measurements.

The rheological changes during the drying period are analyzed from estimations of the changes in solvent balance as the drying proceeds and subsequently the changes in viscosity and solubility power of the remaining solvent. The theory predicting the evaporation behavior of solvents has been reviewed in order to include also the evaporation of water from coating products and hence evaluate viscosity changes with evaporation in aqueous coatings.

1. Introduction

Surfaces are usually coated by applying the fluid coating material in a thin film on the subject by mechanical means. The applied film should subsequently dry into a smooth solid film. Depending on the flow behavior in the application the evenness of the film may vary substantially. In the subsequent drying period the film tends to level into a smooth film. In the same period the film is also prone to develop defects disturbing the protective and estetic qualities of the coating.

The physics of these most common flow problems have been analyzed in detail (A). The flow problems are shown each to be described in a meaningful way in terms of general physical parameters - flow inducing forces and rheological properties. The flow inducing forces - mechanical forces of the application equipment, gravity, surface tension, and surface tension gradients - are either invariable or of casual nature when causing problems. The flow properties are, therefore, crucial in ensuring the right flow behavior in the application process. The significance of the different flow properties has been analyzed with respect to the application process and means of characterizing these are presented (B, C, E). Because of the complexity of the application processes as well as of the coating material the relations between the characteristics and actual flow behavior are ultimately tested on a number of practical cases (C, D, G).

The rheology of coatings with respect to application has traditionally been characterized from measurement on the coating ready for application. In this study the significance also of the flow properties in the drying stage has been stressed.

Means of describing the evaporation and change in viscosity with evaporation are available to a reasonable extent for conventional solution type coatings and are easily combined in a meaningful way (C, D). For aqueous and other potential environmentally

favourable coating types these relationships are not equally well known. The physics of the evaporation process where water is included has, therefore, been analyzed, extending the validity of existing techniques describing the evaporation from coatings (F).

The ultimate value of rheological insight and measurements with respect to the coatings application process is to connect the practical flow behavior to the composition of the coating material. The practicability of this approach is demonstrated on a single aqueous coating system (G). From this investigation and the analysis of evaporation (F) qualitative means of controlling the viscosity development during drying appears.

This report does not intend to summarize the results of the reports and articles on which it is based, but to interrelate the different problems being studied. For the detailed results in the single problem area the reader is referred to the specific articles and reports.

2. Film Defects (A)

The majority of flow problems in coating films in their drying stage are those of leveling, bubbles, foam, convection cells, fat edges, and sagging. Because of the physical nature of flow of these problems, it should be possible to describe them in a common physical framework, thus elucidating the interrelations among the single problems.

2.1 Application and Leveling

Considering only mechanical means of application a number of methods are used to apply fluid coatings on a subject. The main principles are brushing and rolling in manual application, and spraying, dipping, roller coating (calendering), curtain coating in industrial application. During application the viscosity should be of the order 50-350 mPa s, varying with type of coating and method of application (1, 2).

The application methods generally impose a shear rate of some order on the coating material. In brushing it is of the order 10.000 s^{-1} (3, 4) and goes up to more than $1.000.000\text{ s}^{-1}$ in airless spraying (5, 6, 7).

The degree of unevenness of the surface due to the application strongly depends on the rheology of the coating material and on the method of application. The mechanism of brushmarks as well as the film profile behind edge spreaders is described by Smith, Orchard and Rhind-Tutt (8). The surface profile following application by hand rollers has been investigated in relation to the rheology of the coating material by Glass (9) and by Dormon and Stewart (10). Pearson (11) has analyzed the film profile beyond industrial rollers and spreaders. The viscosity of the material in the application situation is found to be very important in all cases. In the case of application methods, where large shear stresses are released before the film is formed, as in spraying,

elastic properties also become important. Elasticity is found to influence the atomization in spraying (12, 13, 14) and roller spatter in hand roller application (9). The primary concern about the film profile is that of the dry film and very little work has, therefore, been carried out on the initial profile after application.

After application, the load on the film is limited to gravity and surface forces. The surface tension tends to smooth the film surface, i.e. induce leveling. The driving force in this mechanism has been calculated by Orchard (15). For a typical case this stress is evaluated to 50 Pa right after the application (16). In the same example Quach and Hansen (16) calculated the stress caused by striations in the dry film to be of the order 5 Pa. Similarly Lin (17) finds 3 Pa. For high gloss products the ultimate stress might go even lower. A number of estimations have been given for the prevailing flow rate in the leveling process. These includes $50-100 \text{ s}^{-1}$ right after application (16), 0.5 s^{-1} as representative for the process (18) and further over $0.5-0.1 \text{ s}^{-1}$ (19) and $0.1-0.01 \text{ s}^{-1}$ (20) down to $0.01-0.001 \text{ s}^{-1}$ (21, 22).

In the stress analysis Orchard shows that the gravity adds very little to the leveling at small film thicknesses as in coatings.

Orchard (15) has analyzed the leveling process in general for a Newtonian liquid and found that the half time, $T_{\frac{1}{2}}$, for the disappearance of the amplitude of a given unevenness follows the proportionality expression:

$$T_{\frac{1}{2}} \sim \frac{\eta \lambda^4}{\gamma h^3}$$

where η is the viscosity, λ the width of the unevenness, γ the surface tension, and h the film thickness. This relationship is widely confirmed.

2.2 Bubbles, Foam

Bubbles in coating films may originate from bubbles in the coating to be applied; they may result from the application procedure or they may be formed during the drying of the film. Only bubbles resulting from the application are related to the flow properties of the coating. The others are related purely to either the chemistry of the coating or the mechanical design of the application equipment and procedure.

By brushing and roller coating bubbles may be formed on top of the applied film as the paint releases from the brush or roller and is stretched into a thin membrane on top of the main film. The conditions for such a behavior are discussed in relation to foaming in the next section.

By spray application the impact of spray drops on the paint film may cause bubbles. A possible explanation of this would be that the bubbles were formed by the interstices between the single drops creating the film. Bell (23) shows, however, in an excellent mainly photographic investigation that the spray drops are flattened by the impact and that the bubbles are much larger than the interstices would be. Bell shows too, that a possible mechanism for the creation of bubbles is splashing of the droplets hitting the wet film. The impact of the drop forms a crater in the fluid surface and at the same time a high rim of liquid rises above the surface. The rim can close completely over the crater entrapping a pocket of air. Bell reaches this conclusion mainly from observing the creation of bubbles by the impact of 3 mm Ø drops on a deep fluid with a speed of 6.9 m s^{-1} . This experiment is made covering the viscosity range 0.7-50 mPa s (cP) and the surface tension range 29-78 mN m⁻¹ (dyn cm⁻¹) by mixtures of xylene/water and corn sirup and by surface active material. By viscosities exceeding 50 mPa s the craters do not close. High surface tension just gives the bubbles a flattened appearance. The diameter of the bubbles is approximately seven times that of the drops, which also is the case in spraying.

Relating these observations to spraying of drops of diameter 10-100 μm means comparing two situations of widely different momentum of impact as the momentum of the drops increases with the third power of the diameter of the drop and the impact area only by the second power. Photographs taken of the film surface during spraying indicate a similar behavior at those much smaller dimensions (23).

The formation of bubbles by spraying can be minimized by a fine atomization and a low speed, both giving a smaller momentum of impact. This is in accordance with normal practice of minimizing the tendency to get bubbles in sprayed films by increasing the spraying distance and by the correct choice of nozzle and spraying pressure (24, 25). It should be remarked, however, that a finer atomization gives a larger drag than a coarser atomization (26) and a lower pressure, therefore, does not necessarily give less bubbles.

A low surface tension of the material is found to support a fine atomization (12, 27). Low surface tension due to surface active material is reported to be unimportant in this respect, though, because of the speed of the formation of surfaces (28) and the numerical interval of the surface tension for materials for coatings is not very wide. A low viscosity also supports the atomization (12, 27, 28, 29), but supports the formation of bubbles as well, according to Bell.

The release of bubbles from the paint film is found to be improved by delaying the viscosity increase in the drying period irrespective the orientation of the film with respect to gravity. No straight forward description of the bubbles release is apparent, but the volume decrease of the film in the drying seems to be an important factor.

The emerging bubbles may be retained as a foam membrane on top of the film because of interaction between the surface of the bubble and that of the coating film due to the presence of components with special affinity to surfaces, i.e. surface active material.

If a bubble once formed does not burst instantaneously the bubble membrane will slowly be drained because of the surface tension tending to give surfaces a constant curvature, thus resulting in suction toward the intersections of bubble and film surface. This suction is opposed or promoted by the gravity depending on the orientation of the film. Foam membranes may be classified into two main categories according to their drainage behavior, "rigid" or "mobile", where the drainage is very slow in rigid membranes compared to mobile. The difference in drainage has been shown to be associated with the type of the monolayer on the surfaces of the membrane (30). The rigid membrane possesses close-packed, rigid monolayers whereas the mobile has monolayers with low viscosity. Physically the surface layers may be associated with a surface viscosity or surface rheology independent of that of the bulk fluid.

If the membrane withstands thermal and mechanical disturbances from the environment until its thickness is reduced to about 0.1 μm , different molecular forces start acting within the membrane. This is first the electrostatic repulsion of the similarly charged surface opposing the drainage. Then also the van der Waals attraction tending to accelerate the drainage becomes significant and finally the steric hindrance of the surface layers tend to stop the drainage. The electrostatic repulsion and the steric hindrance may both lead to a metastable membrane, but is found only when the membrane is protected against external disturbances.

The foam membrane in the coating film will, therefore, either have solidified with the drying or burst due to external disturbances before it is drained that far.

The degree of deformation of a bubble membrane following from a given disturbance may vary with the nature of the surface layer. The thickness where the membrane becomes sensitive to disturbances following from normal surroundings will, therefore, vary. A significant factor here is an elastic behavior of the membrane, where a deformation generates a force tending to restore the even thickness of the membrane. This elasticity is caused by

the higher surface tension of the surface area created by the disturbance, compared to that of the surrounding surface area. This surface tension gradient will initiate a movement of the surface active material on the surface towards the higher surface tension spot (the Marangoni effect). With the viscous material transport following the surface transport, the membrane thickness is restored. This surface transport of surfactant molecules is active only if the diffusion of surfactant from the interior of the membrane is slower (30, 31).

The stability of foam in coatings is thus physically mainly related to surface viscosity, surface elasticity, and also bulk viscosity. To break foam in coatings disturbances may be incorporated in the coating product as discussed in the section on craters.

2.3 Convection Cells

Convection cells have been shown to be due to decreasing surface tension down through the drying coating film (32). The surface tension may vary through the film because of the evaporative cooling of the surface and in the last stages of drying also because of compositional gradients. Density gradients of the same origins may also cause convection cells (33), but this effect is unimportant in films of small thicknesses as coating films (32, 34).

When small disturbances locally cause a deeper layer to become part of the surface, a surface tension gradient is created. Gradients in the surface tension appearing along the film surface will give rise to flow. These gradients tend to even out by stretching of the zones of initial lower surface tension, whereby bulk material will follow the surface motion because of the viscous nature of the fluid. The resulting deformation of the surface will either level out again or the flow will continue by carrying still deeper layers to the surface, thus starting a convection cell (Bénard cell), with return flow deep in the film because of surface tension smoothing out the surface.

This convective stability problem has been analyzed in some detail (32, 34, 35, 36). The stability depends on the Thompson number N_{TH} for the film:

$$N_{TH} = \frac{\sigma \beta d^2}{\rho \nu \kappa}$$

with

- σ coefficient of thermal surface tension change, $\frac{\partial \gamma}{\partial T}$
- γ surface tension
- β temperature gradient through the undisturbed film
- d film thickness
- ρ density
- ν kinematic viscosity
- κ thermal diffusivity

When the Thompson number exceeds a critical value for stability a disturbance of the film surface will grow into a stable convection cell.

The critical limit of the Thompson number for which convection cells will occur is, furthermore, extremely strongly influenced by the presence of surface active material, i.e. of surface elasticity (37).

2.4 Fat Edges

At the edges of the coating film an extraordinary film thickness, "fat edges", may appear. This problem is also a result of surface tension gradients. Because of the surface tension tending to minimize the surface area, the applied film initially has a gradually decreasing film thickness at the edges of the film. Since less volatile material will evaporate from the thinner areas of the film, the drying proceeds faster here and the evaporative cooling becomes different from the main area of the film. The surface tension, therefore, may become higher at the edges leading to flow toward the edges.

Such a situation, caused by concentration differences, is analyzed by Weh (38). The temperature influence generally seems to be more important since coatings usually contain surface active materials. The appearance of fat edges is also related to the development in viscosity in the drying period, since the development in viscosity is determining for the extent of edges developed in the early stages of the drying as well as for the subsequent leveling.

2.5 Craters

Small holes or depressions may appear in the applied coating film in the drying period. Such craters are also due to surface tension gradients appearing when a drop or particle of low surface tension comes into contact with the film surface. Such drops and particles may originate both from contaminations in the surroundings and from the coating material. For example surface active material may have been added to the coating in a concentration exceeding the solubility limit, whereby the drops of the surfactant act as an anti-foaming agent by causing craters in the foam membranes.

When cratering does occur, however, only the craters remaining in the film disturb the quality of the coating, and only very few craters become permanent compared to the number created. With a sufficiently high viscosity, the material flow due to a surface tension gradient will be very slow compared to the diffusivity of the surfactant and the drying of the film, and in the case of low viscosity the crater is easily formed, but levels subsequently. Craters are reported to be formed with a relatively high shear rate (39) indicating a shear stress of some size.

Craters becoming permanent in the coating film, therefore, are created at an intermediate stage, where the viscosity is low enough to permit craters to be formed, but too high for the subsequent leveling or leaving too short a time for this leveling.

2.6 Sagging

On vertical surfaces coating films tend to flow downwards due to the gravity. Each single layer through the film is forced downwards by the weight of the part of the film area more distant from the substrate than the regarded layer. This stress has the size of $F = \rho g (h-y)$, with the density ρ , the film thickness h and the distance of the regarded layer from the substrate y . Patton (21) has calculated this stress on the interface of a typical paint film to 0.8 Pa. For a Newtonian liquid the surface velocity becomes:

$$v_0 = \frac{1}{2} \frac{\rho g}{\eta} h^2$$

where η is the viscosity of the film. The flow field varies, however, substantially with non-Newtonian properties of the coating. Since the stress varies through the film a shear thinning material will get another flow field with dominating flow deepest in the film, and in a coating being solid at stresses below a yield stress no flow will occur at all in the top layers of the film.

Sagging of a film with a perfectly smooth surface will not disturb the appearance of the surface. The flow velocity varies, however, strongly with the film thickness and a small disturbance on top of the film is shown (40) to move twice as fast as the film surface itself. Unevennesses in the coating film, therefore, capsize as the sagging proceeds, thus developing into curtaining which disturbs the quality of the final film.

Since the density of the coating may be varied only with a very narrow range, the extent of sagging is determined by the viscosity of the film during the drying period only.

2.7 The Defects and their Interconnections

The flow inducing forces in the application methods considered are of mechanical nature. In the drying period they are either gravitational, surface tension or surface tension gradients.

The leveling is due to the surface tension, tending to minimize the surface energy. The surface tension of coatings is restricted to a relatively narrow range, since the typical range for resins is $30\text{--}45 \text{ mN m}^{-1}$, for organic solvents $25\text{--}35 \text{ mN m}^{-1}$, and for surfactants typically just below 20 mN m^{-1} with fluorinated types down to 11 mN m^{-1} . This variation range does not effect the leveling significantly. The surface tension of coatings containing water (surface tension 72 mN m^{-1}) is always reduced by surfactants. The numerical value of the surface tension may, however, have a significant influence on the size of the surface tension gradient following a contact of low surface tension material to the surface, causing craters. The density interval for a given product type is also rather limited and the problems of sagging and leveling are, therefore, determined by the rheology.

The surface tension varies with the concentration of solvent in the coating film because of the different surface tensions of the components of the coating. The surface tension is also sensitive to temperature and the evaporation of solvents may, therefore, lead to surface tension gradients giving rise to convection cells and fat edges.

The presence of surface active material on the surface will depress the concentration dependency of the surface tension, but not necessarily the temperature dependency, since the temperature influence mainly is related to the volume occupied by the single molecule at different temperatures.

When surface active material is used in the coating, some time will pass after the application before equilibrium is reached between the concentration of surfactant in the coating and on the newly created surface area. This time depends on the amount and mobility of the surfactant in the coating.

In the period until the surface has become saturated with a given surfactant, the surface will be sensitive to cratering by this surfactant, if it has a lower surface tension than the surface and if it is present in the film as drops or micelles and, furthermore, to any drop or particle of lower surface tension reaching contact to the surface either from the environment or from inside the film. The general sensitivity of the film to cratering may, therefore, be diminished by a fast saturation of the surface by a low surface tension surfactant completely soluble in the coating.

A fast saturation of the surface by surfactants will also eliminate the elasticity of the surface, which is responsible for the selfhealing mechanism in foam stability. The same effect, however, is often used to increase the critical limit for the occurrence of convection cells.

Drops of surfactant not soluble in the coating, which may cause cratering, are used in breaking of foams. Foam stability is, however, related to a rigid structure of the surface layers, usually due to a close packing of more types of surfactants on the surface, i.e. a high surface viscosity. The electric potential of the surface layers may also add to foam stability. The foam stability may, therefore, be influenced by controlling the packing tendencies and potential of the surfactants involved. The antifoam agents may, anyway, give the desired effect without disturbing the film surface. This may be because the cratering tendency is limited to an early period of the drying, for reasons of drop-size, saturation time, and viscosity increase.

Besides influencing the surface tension and the occurrence of surface tension gradients, the presence of components with different affinities to surfaces thus also influences the viscosity and elasticity of the surface regarded as functions of time after application. All those properties important to the flow behavior in the drying film are related to the following properties of the surface active materials in the coating: the concentration, mobility, solubility, packing tendencies for combinations of

surfactants, and electric potential. The choice of surfactants with different characteristics will depend on the behavior desired and the problems being related to the use of the surfactant.

The quantitative relationships between the sensitivity of a coating product to the different flow problems, the surface rheology, surface tension, and the parameters for the surface active material in the coating film have not been investigated in detail yet.

Since the flow inducing forces in the drying film to a large extent only vary within a narrow interval, as the gravity causing sagging and the surface tension causing leveling, or are of casual nature, as the presence of low surface tension material causing craters, the flow properties of the coating film during the drying are of primary importance to the film quality.

Application is favoured by a low viscosity compared to the viscosity in the applied film. It is carried out under a high flow rate whereas the flow in the applied film is due to relatively small stresses and hence, only to low flow rates.

Leveling is a process described in half times and the major part of the leveling, therefore, takes place in the period right after the application. The release of air is also favoured by a low viscosity in the first time after application, since the bubbles should emerge in time to permit leveling of the mark from the burst bubble. The problems of sagging and curtaining are avoided by a high viscosity. The curtaining is, however, a problem developing with time. The excess local film thickness has to develop by sagging and these disturbances may also have to capsize before the phenomenon becomes visually disturbing. The sagging problem may, therefore, be controlled by a balance of the viscosity early and later in the drying period. The formation of craters and fat edges remaining in the dry film is also sensitive to the increase in viscosity in a period later in the drying. The occurrence of convection cells is favoured by a low viscosity but the appearance of convection cells in the dry film depends on the development in viscosity after the convection has ceased.

The viscosity development during the drying period, therefore, strongly influences the balance between leveling and sagging and will also influence the extent of the other disturbances in the dry film. The optimum viscosity profile could consist of a low viscosity period permitting leveling and air release followed by a steep increase in viscosity through the region where disturbances formed do not disappear, thus, making this period as short as possible and stop sagging before it causes visual disturbances. This description is purely qualitative but shows that the application properties of the coating are influenced strongly by adjusting the drying behavior of the product.

3. The Rheology in Application and Drying

The flow properties of the coating material during the application process have been expressed in terms of the viscosity of the material at the different stages of the process. In the design of coating materials, adequate for specific application processes, the different factors determining this apparent viscosity throughout the process become important.

3.1 Rheological Properties (B)

Considering first only the inert, isothermal coating material, it may respond to stresses partly by flow and partly by elastic deformation. Elasticity is usually referred to as the ability of the material to snap back when the external stresses are removed (41). Elasticity conserves energy by the deformation whereas the flow dissipates energy. Since the material is fluid, the elastically deformed structure in a situation under stress will relax with the time, i.e. the recoverable deformation will decay with time. The material is said to have a fading memory. To influence the flow behavior in the process, the elasticity must have a memory lasting at least a time comparable to that of the rate of changes in the process. Thus the ratio of elastic and viscous behavior of the material depends strongly on the time scale regarded. The ratio between a characteristic time for relaxation of the fluid and a characteristic time for the process is named the Deborah number and is regarded as "a criterion for the importance of elastic effects" (41).

Furthermore, the viscosity and also elasticity of coating materials will often depend on the flow rate because of orientation effects and structure on molecular as well as particle level. Regarding the viscosity this is termed shear thinning or shear thickening. The time required to obtain equilibrium between flow rate and structure/orientation, once the flow rate or stress has been applied is often substantial. This time dependency is termed thixotropy.

The flow rate dependency must be regarded as energy conservation through structures (secondary bonds) broken down, or orientation (entropy), but it is, contrary to elasticity, not flow inducing when external stresses are removed.

Finally, at very small stresses and a given time scale the material may behave either as a Newtonian liquid, where the structure recovers faster than the break down in the flow (42), or as a solid depending on the structures in the material. In the latter case the material can be regarded as having a yield stress, below which no flow will occur. Such nature is termed plasticity.

These basic rheological properties are all interrelated and the rheological properties cannot be expressed by simple material constants or functions in a general equation, relating deformation behavior with stress situation. This can be done only for materials with an especially simple nature or for a simple deformation process.

Furthermore, the rheological properties of coating materials in the application process are functions of the drying. During and after application volatiles normally evaporate from the coating; chemical reactions may also start while the film is still fluid.

Summarizing, the rheological properties involved in the flow behavior of coatings may be expressed by the following material properties and their functionalities:

MATERIAL PROPERTIES	EACH FUNCTION OF
viscosity	applied stress or flow rate (only viscosity and elasticity)
elasticity	time of applied stress (contains the thixotropy)
plasticity (yield stress)	time scale of change in stress changes in material (drying) temperature

Because of these many parameters involved in the rheology of coatings and because of their interrelations, the rheological properties involved in the application process must be evaluated with due consideration to the process itself, as it has been stressed by Weltman (43).

3.2 The Importance of the Various Rheological Properties (B)

When the rheological properties are related to the process described in the preceding text, the picture indicated in figure 1 is found.

Figure 1 indicates the apparent viscosity through the application process, as well as the different factors that influence the viscosity. The presence of plasticity and elasticity will, furthermore, add to the apparent viscosity in specific situations.

In the storage period prior to the application process, the settling tendency of the heavier components of the coating product should be eliminated or minimized. A high viscosity or a plastic nature of the coating in this situation with stresses in the millipascal range, would be beneficial. This is indicated in the figure by the dashed viscosity axis.

In the application itself the viscosity should be of the order 50-350 mPa s. Since the application is usually characterized by the exertion of a shear rate on the coating material, varying from a few hundred reciprocal seconds to more than a million, this may be compatible to the storage requirements if the coating is shear thinning or plastic. A yield stress preventing settling will not influence the flow at these high shear rates.

Elastic properties of the material may influence the application significantly, since high flow rates are applied to and released from the material within short time intervals. In relation to spraying Golding and coworkers (44) have shown that elasticity should have a stabilizing effect, thus making the atomization

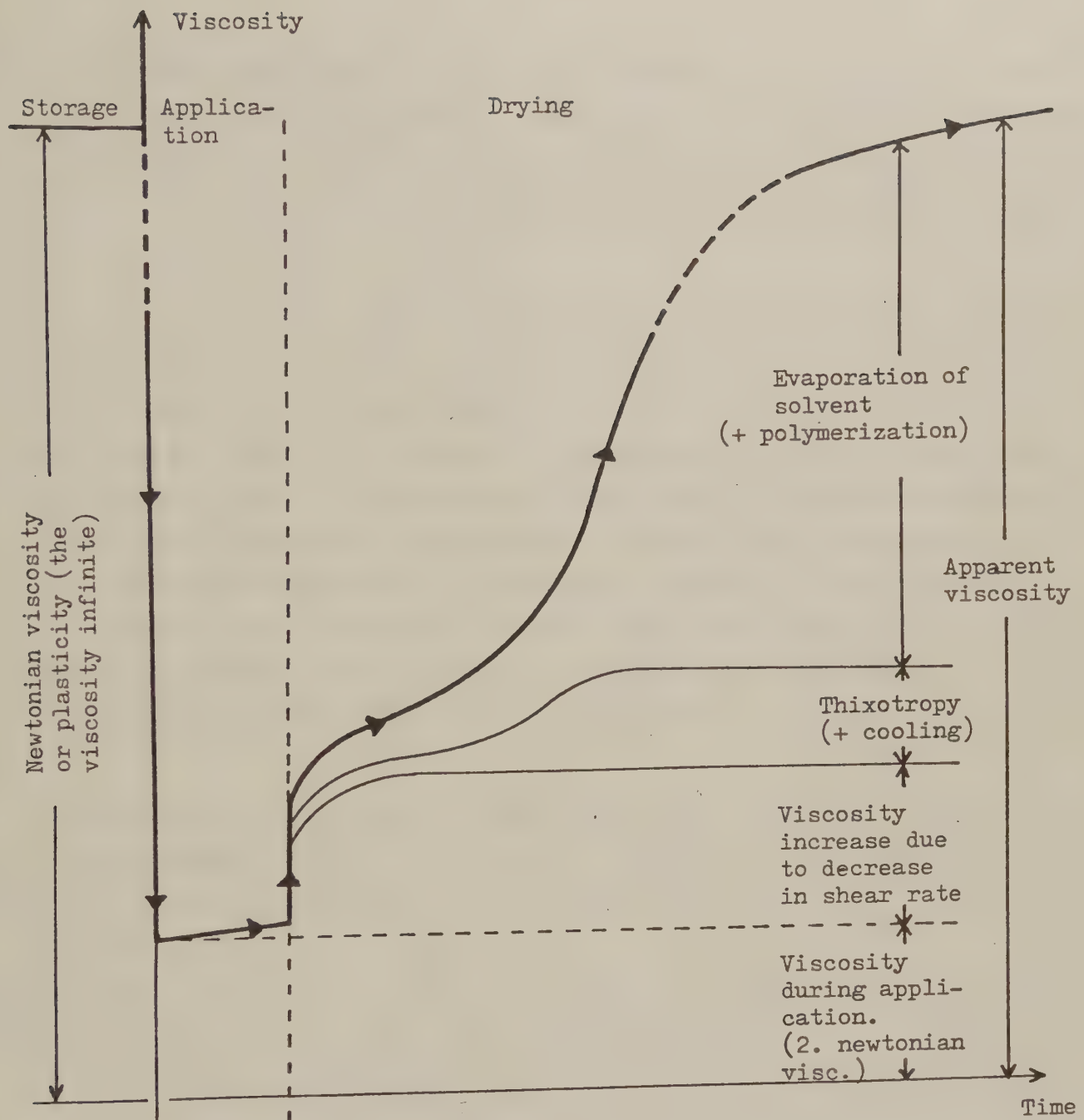


Fig. 1. Viscosity of a coating during application and film formation, in principle. During storage the viscosity is very high or infinite due to plasticity. Under application large shear rates lead to a low viscosity due to shear thinning. By some application methods there are an evaporation during the application and termination of external deformation before the application is completed (spraying, curtain coating).

During drying the flow is induced by relatively small forces due to surface energies and gravity. Shear thinning results in an immediate increase in viscosity as the application is completed. As the film levels the stresses decrease and the viscosity is further increased. Time dependent recovery of structure and random orientation after the application shear rates (thixotropy) increases the viscosity in a period after the application. A temperature decrease due to evaporative cooling is expected to be of the same form. Gradually the evaporation and eventually also beginning polymerization will be responsible for the continued viscosity increase till the film solidifies.

more difficult, while Fraser (45) finds a more even atomization with elastic than with non-elastic properties of the material. Those findings are in agreement, since the elasticity both prevents creation of spray dust between the primary droplets (46) and makes the splitting up more difficult.

The initial surface profile, as the film has been applied, has not attracted very much research interest, since the practical concern is the profile of the dried film. Hence not very much is known of how elasticity affects the application itself. Khanna (18) indicates that an elastic component will give a recovery of the striations from brushing right after application. In the hand roller coating process Glass (9) has studied how rheology effects the release of the film behind the roller. Here the elasticity is found to interfere with the creation of drops from filaments between the roller and the substrate. For such reasons, elasticity should be included in the evaluation of rheological properties of coating products.

If the material has a shear dependent nature, the viscosity increase subsequent to the application will be influenced by the change in flow rate in this period. In the case of a shear thinning material, the viscosity will increase momentarily, when the application has terminated, and increase further as the surface stresses diminish with the leveling. If the material is thixotropic as well, the recovery of viscosity after the break-down of structure in the application will also add to the viscosity increase in the first period after application. The advantages of shear thinning in the drying period are consistent with the requirements in the storage period.

Since the stresses in the drying period are of limited size, the presence of a yield stress for the coating material may influence the flow significantly. If the yield stress is higher than the stresses caused by the curvature of the film surface, no leveling will occur or it will terminate before the desired smoothness is obtained.

Conversely a yield stress has an analogous but positive effect on sagging as described by Fredrickson (47) and by Patton (48) for a Bingham liquid. Since the stresses associated with both storage and sagging are smaller than those occurring during leveling, a yield stress of moderate order may be used in the control of the flow behavior in the process.

The flow in a viscoelastic film has been described by Bierman (49). His analysis show that elasticity will have a retarding influence on leveling, although the effect is less important than that of viscosity. Glass (9) relates this observation to leveling of coatings by correlating the final surface profile to the recovery of elasticity after application. Long recovery time means good leveling. Khanna (18) finds that leveling improves with increasing elasticity. Both these findings relate to the entire process of generation of striations and leveling. Those investigators and others as well (17) show that elasticity plays some role, since the viscous characterization is insufficient to correlate data.

The importance of elasticity in flow seems to be more questionable than in the application, since the Deborah number is much lower afterwards and a recovery of elasticity after higher shear rates is also involved.

The last and final increase in viscosity is due to the evaporation of volatiles of the coating. A chemical curing may also be initiated before the film has solidified. The evaporation also implies a cooling of the film, thereby initially increasing the viscosity until a quasistationary temperature is reached.

All the rheological properties and parameters listed in the preceding section may thus be significant in the application process. However, not all coating materials are that complicated rheologically; many coatings are Newtonian liquids.

With all those rheological properties, differently involved in the different stages of the coatings application process, being available in the design of the coating product, a satisfactory

flow behavior may be achieved in several different ways. A characterization of the different properties will indicate how a product can be modified to achieve the desired flow behavior throughout the entire process or just to ensure that the requirements are met. However, no single measurement or series of measurements is able to reflect this behavior because of the number of properties and interrelations involved.

When characterizing rheological properties significant to the application process, one approach would be to characterize the rheological properties of the coating product, before changes in the material take place, and to follow the material changes in the process. A characterization of the several rheological properties as the material changes must be reserved for specific problems because of the span of such a task. A measure of the actual behavior of the material in the process in terms of apparent viscosity, however, is considered to be essential in order to assure that the sum of rheological properties gives the desired flow behavior or, inversely, to establish whether a flow problem is related to the rheological properties of the material.

Applying these arguments on the coatings application process, the following quantities should be measured:

- The apparent viscosity throughout the process.

- The viscosity before drying, reflecting its dependency of flow rate or applied stresses (shear thinning) as well as its time dependency after changes in flow or stress (thixotropy).

- The yield stress.

- The elasticity.

- The change in material until solidification.

Plasticity and elasticity also depend on the previous treatment of the coating material, but since they in many cases are of minor importance compared to the viscosity, they should be measured in the full functional range only in specific situations. The temperature is also disregarded as a parameter in the general characterization, since the viscosity change with evaporative cooling is expected to be very similar for broad ranges of coating types.

The properties to be characterized are functions of a number of parameters not included in the characterization. The choice of experimental principles and techniques, therefore, has a decisive influence on the relevance of the measurements.

3.3 Rheological Characterization Prior to Application (B)

The measurements on the coating material are confined to be in shear flow, since elongation viscosity at low viscosities, as for coatings, is not technically measurable. This leaves the few elongation dominated application methods as airless spraying and roller coating beyond the characterization since shear and elongational flow behavior are not related in a simple way. In the measurements coaxial cylinders have been preferred due to the minor impact of evaporation in measurements with this type of geometries.

The shear rate dependency of the viscosity is measured by determining the viscosity with geometries covering both the low shear and high shear rate regions. In practice shear rates between 0.1 s^{-1} and 25.000 s^{-1} are easily covered. This low shear rate is not necessarily low enough to determine whether the coating material possesses a Newtonian or plastic nature at low shear stresses but it does cover the major part of the shear rates important for the flow in the applied film. The high shear rate covers the rates occurring in most of the application processes and may also be extrapolated to some extent when shear thickening is not expected, e.g. from dense packing of particles.

The shear rate measurements are made in equilibrium between shear rate and shear stress, thus not taking a hysteresis resulting from a certain increase in rate and a subsequent decrease as a measure for thixotropy. This is because of the difficulty in evaluating the degree of thixotropy from a hysteresis area since this is also determined by the shear rate range covered and the rate of change in the measurement. The thixotropy is characterized by determination of the transient viscosity change following a change in shear rate. Only one change in shear rate is followed and for reasons of

reproducibility the recovery of structure is followed rather than the break-down. For reasons of comparison to the application process it is followed over a shear rate change as large as possible.

Elasticity is characterized by a transient measurement, since measurement of normal stresses or phase shift in oscillatory measurements is very resource demanding, both in instrumentation and measurement. The elasticity is characterized by the stress decay after cessation of one low shear rate. The stress decay measurement is chosen for reproducibility reasons and since it is closely related to the cessation of application in the application process. Measuring from a low shear rate gives the largest measurement response, which is important at the low coating viscosities. Measurement is made from only one shear rate level as elasticity is of second order compared to viscosity in coatings.

Plastic yield is characterized by the same measurement, since the stress decay will cease when a yield stress is reached. This will be a dynamic yield which will also depend strongly on the prior shear rate and the rate of decay in stress, but with the low shear rate a close relationship to the application process is obtained. A determination of a static yield stress from following the stress development when a low shear rate is applied on the coating material is not possible because of interference of thixotropy in the preparation of the measurement.

The shear rate change in the thixotropy measurement is rather restricted on common versatile viscometers and the torque registration slow compared to the stress decay in order to get a stable registration. Furthermore, the inertia of the driving system may only be excluded by a manual brake. In order to relieve these limitations to the characterization, the manual shifts for the rotation speeds and for the torque registration ranges, the electrical damping of the torque registration as well as the brake were connected to relays controlled by a desk calculator. The external ports of the viscometer determining the rotational speed and giving the measured torque by each an voltage were both inter-

faced to the same calculator. From these modifications and a suitable software package the instrument was capable of performing the thixotropy measurement with a shear rate change of 2 to 4 decades depending on the degree of shear thinning of the material. Relaxation measurements are found to be reliable after less than 0.5 s and with a resolution better than 0.06 s.

By means of the calculator the induced rotational speed and the registered torque are directly converted into shear rate and shear stress and all three measurements are performed by the calculator with input only of the parameters of the measurement.

The measured data may, furthermore, be compared to different mathematical models. The shear rate measurement may be compared to models of generalized Newtonian types and to quasilinear viscoelastic types. The thixotropic recovery and the stress relaxation are related to models of an exponential change. The viscoelastic models are related to the measurements by curve fitting and the others by linear regression. By the linear regression the significance of the mathematical approximations may also be determined. The curve fitting is applied to the more complicated mathematical models and the success of the curve fitting may depend on relevant first estimates for the coefficients and a reasonable fast convergence.

By applying simple models to the measurements, the material may be characterized by a few coefficients instead of a number of curves, provided that an acceptable fit is obtained between model and data. Different simple models are often found to describe the material in the measured range sufficiently accurate from a technological point of view. No one of these simple models are, however, found to be of general validity to broader ranges of coating materials.

From the rheological model the validity of the measured results may be extended, e.g. the stress relaxation and yield stress and the thixotropic recovery may be estimated at different shear rate levels from the single one measured.

The rheological models are each related to one of the measurements. One rheological model encompassing these three models could be a support in the elucidation of the interrelations of the different rheological parameters defined in the next sections. Viscoelastic theory may only be related to the discussed rheological parameters if thixotropy is regarded as an elastic property in contrast to what is discussed earlier and if the plasticity is regarded as a very slow stress decay. This last description would unify the opinions of the existence/non-existence of solid behavior of coatings at low stresses. With those assumptions the material may most simply be described by an extended Jeffrey element containing 3 Kelvin elements, i.e. one short relaxation time for the elastic behavior, one longer for the thixotropy and one very long for the plasticity. This model may be solved for the three considered measurement flows and should be able to show if the assumptions are valid or the thixotropy should be regarded as a rate process superimposed to the viscoelastic behavior as Brodkey has proposed (50). It will, furthermore, show whether the simple linear assumptions for each of the properties are sufficient. If such a description covers the regarded materials in all of those very different measurement flows, the coefficients from those measurements characterizing the material may then be used to describe the behavior of a material in other flow fields, e.g. in elongational flow as present in roller application and in the flow in a spray nozzle.

3.4 Viscosity in the Drying Period (C)

The total of the contributions to the viscosity during the film formation is measured by a method based on the original definition of viscosity. A plate is drawn over the drying film at different times with a shear stress of approximately 25 Pa as representative for the leveling process. The methods differ from the definition by the fact that the plate has edges and a mass. In order to avoid squeezing the plate into the film, the plate is given a net normal force away from the substrate and the front edge is bent away from the film. In practice the measurement can be performed simply by

pulling a micro slide ($2.6 \cdot 7.3$ cm) over the paint film by a small weight (e.g. 5 g) hanging over an easily running pulley, measuring the time for the motion over a practical distance. Other methods have been used to characterize the apparent viscosity during drying but this method is preferred because of its similarity to the practical situation and because it is quantitative.

To evaluate the method, the viscosity of different Newtonian oils was determined from such measurements and the definition of viscosity.

Comparison of viscosity determinations on Newtonian oils by the sled method and other methods. The film thickness by the sled method: 80-100 μm .

Oil	Höppler	Rotovisko	Sled
A	0.36	0.36	0.44
B	0.44	-	0.45
C	1.41	1.38	1.38
D	3.75	3.77	3.72
	Pa s	Pa s	Pa s

Measurements on the Newtonian oils over different distances, but otherwise identical, showed that measurement over the first centimeters were most stable. The acceleration of the plate at the start of the measurement does not appear in the measurement - since it is very fast - and problems of squeezing have not developed to a degree interfering with the velocity of the sled. Measurements with different film thicknesses show a variation of less than 10% from 40 μm to 130 μm . The sled measurements are conducted in an open room to allow for drying. Thus the temperature influences the accuracy of the method.

3.5 Evaporation

The evaporation from the drying coating film is characterized simply by the weight loss relatively to the solid content of the coating material.

Coatings usually contain a number of different volatiles and the impact of the evaporation will be due to changes in solubilizing power and in viscosity of the volatile mixture as well as to the decreasing amount of volatiles (C, D, F). When coating materials with non-identical volatile content are considered, those two additional factors must also be taken into account.

For coating materials with ideal interaction between volatiles and polymer (true solutions), the volatile balance as the drying proceeds may be evaluated sufficiently accurate technologically from simple isothermal mass transfer considerations in air, based on evaporation data for the single volatiles, available in tables (51, F). From the volatile composition known through the drying period, the changes in viscosity and solubilizing power of the mixture may be evaluated by a volume average over the single components (52, 53, 54, 55). The viscosity of the mixture may thus be plotted as function of the remaining amount of volatiles and, by expressing the solubilizing power of the volatile mixture by solubility parameters, the change in solubilizing power may be expressed as a scale in a usual solubility parameter diagram and thus directly compared to the solubility of the resin. A marginal solubility is expected to increase the viscosity in solutions at high concentrations, but when effectively inside the solubility area this effect may be minor compared to the increase in viscosity with increase in the viscosity of the volatile mixture.

3.6 Experimental Results

Returning to the characterization of the rheology of coatings in relation to the application process, it consists of the 5 measurements indicated in figure 2.

The rheological measurements prior to application may be exemplified by the following measurements on a flat, white wall paint shown in figure 3A, B and C.

Figure 3A shows that the paint has an adequate application viscosity, since the viscosity at high shear rates is of the order 100 mPa s. At low shear rates the viscosity is extremely high, indicating bad leveling characteristics. Figure 3B, however, indicates some degree of thixotropy in the first half minute after application during which the viscosity will be lower than the equilibrium value. In practice this period may be more than half a minute since the recovery is measured from only 700 s^{-1} and the viscosity curve indicates that structure is not totally broken down at this shear rate lower than the application shear rate. The stress relaxation curve (figure 3C) indicates that the paint has a yield stress of the order 4 Pa right after shearing at 7 s^{-1} ceases. This measured yield stress is comparable to the stresses in the film surface responsible for the leveling, thus indicating that no leveling will occur in the applied film. The yield may be higher after a little longer time, since the thixotropic recovery indicates that the paint recovers structure for some time after application. In a practical test this paint was found to be easily applicable, but with no leveling at all, confirming the results from the measurements. From the stress relaxation curve it is seen that the paint may possess some elasticity, but this is not expected to influence the relatively slow application processes, brushing and hand rolling, considered here. Since this paint did not flow at all, the drying period becomes unimportant with respect to flow.

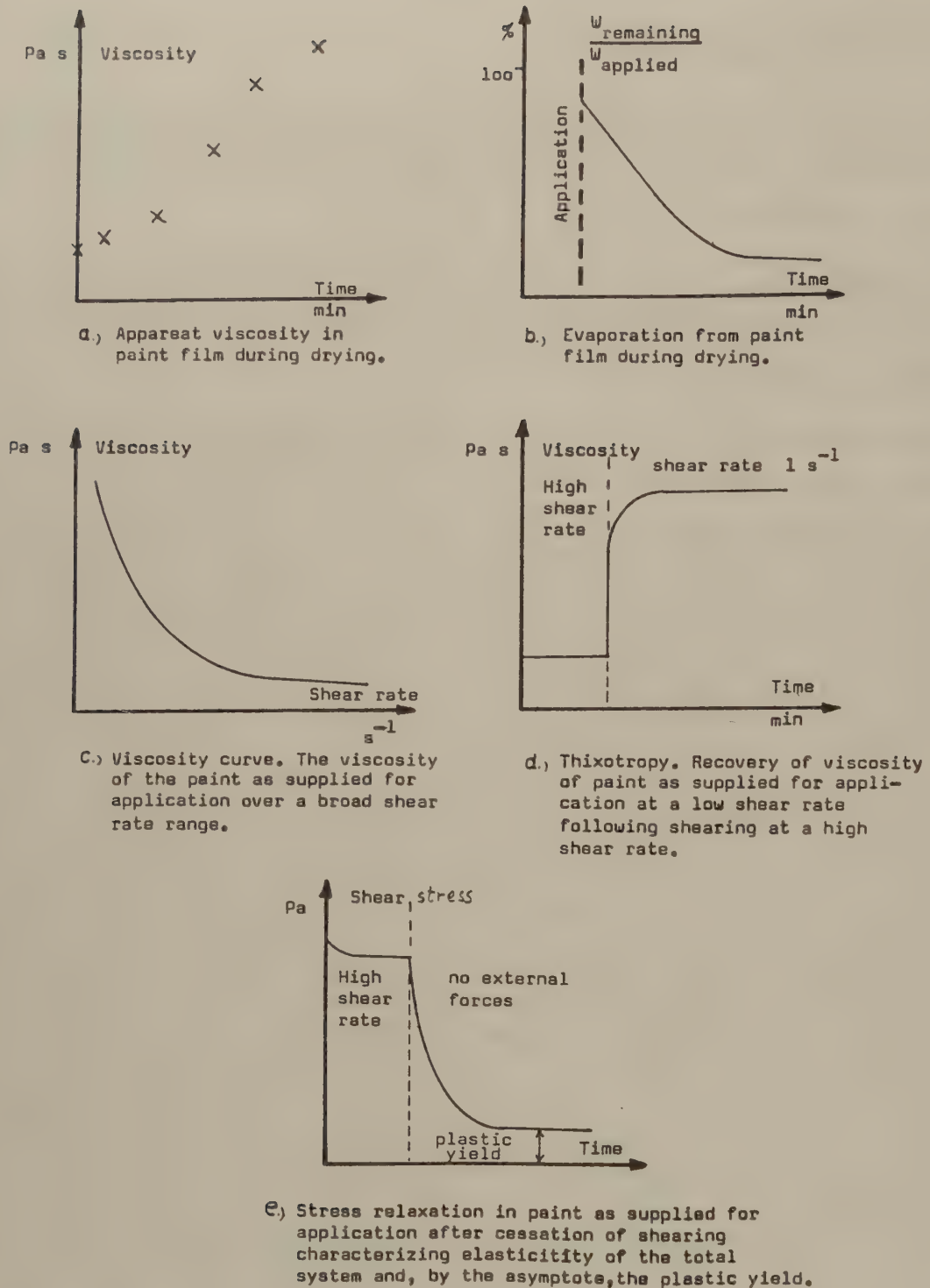


Fig. 2. Set of curves to characterize the rheological behavior of coatings in relation to application and film formation.

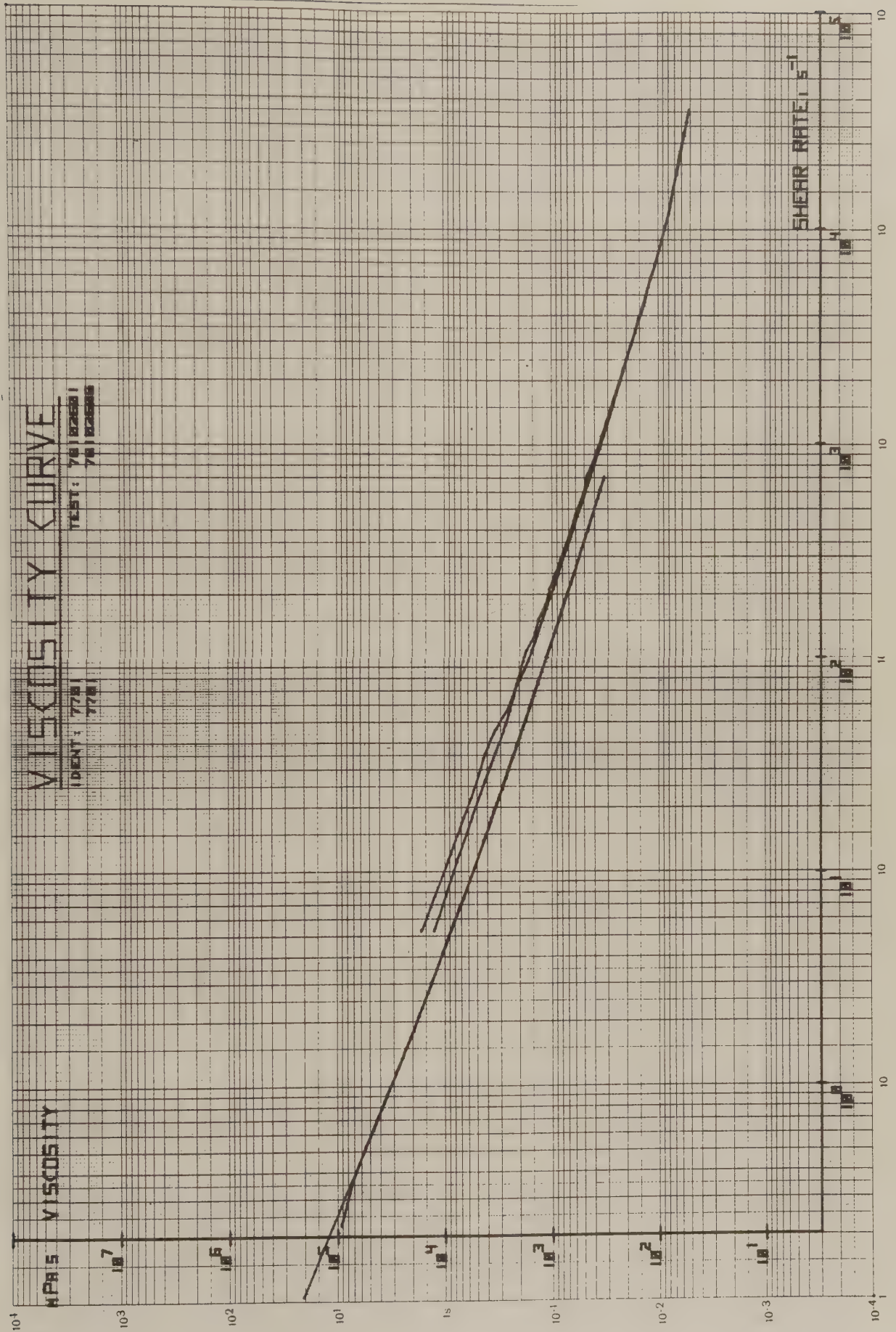


Fig. 3A. Characterization of the rheology prior to application for a flat, white wall paint.

Equilibrium viscosity covering the shear rate range from $0.1 s^{-1}$ to $35.000 s^{-1}$. The deviation between the two measurements is due to the calibration of the instrument.

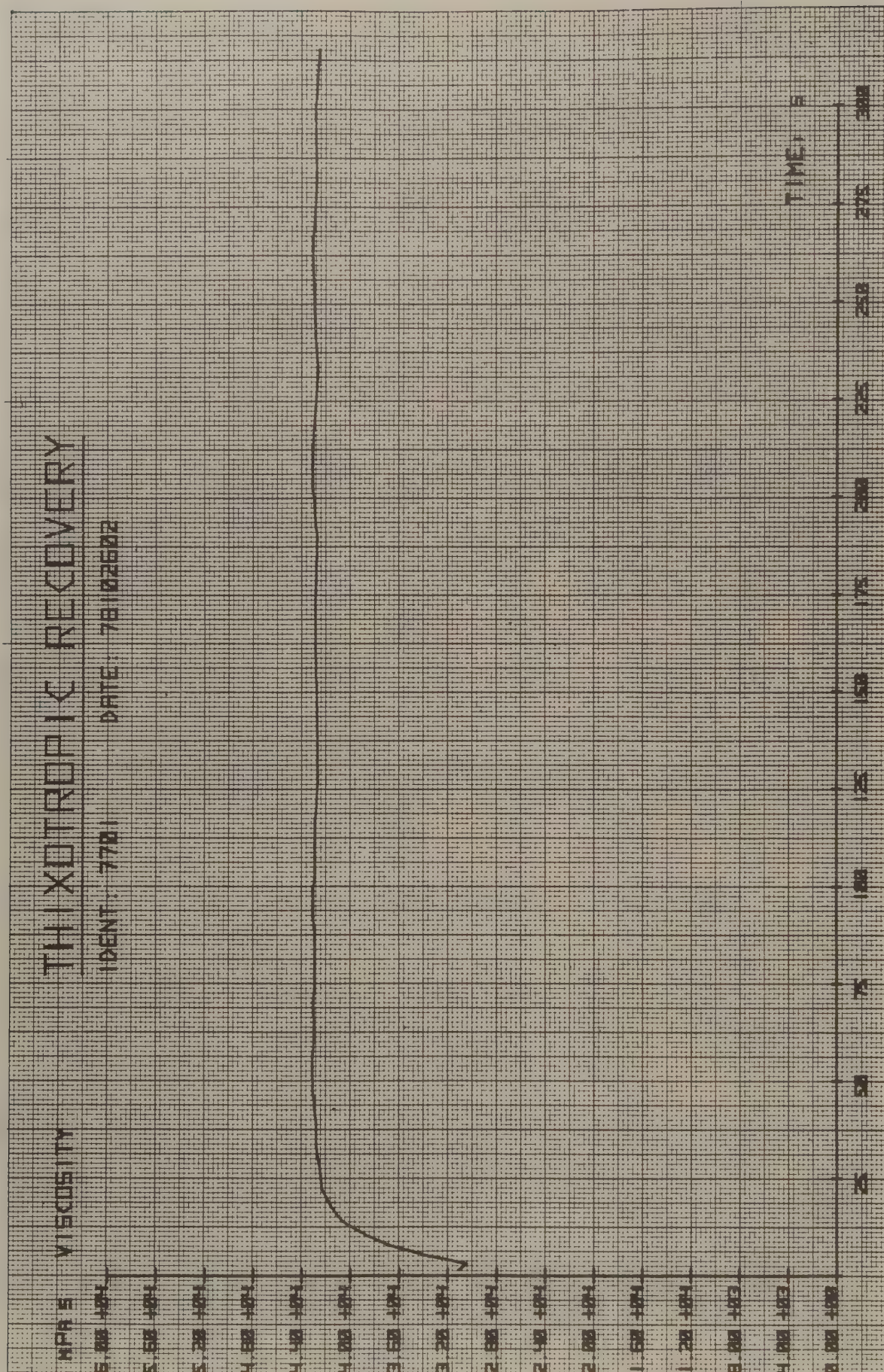


Fig. 3B. Characterization of the rheology prior to application for a flat, white wall paint.

Thixotropic recovery at 0.7 s^{-1} after structure has been broken down at 698 s^{-1} .

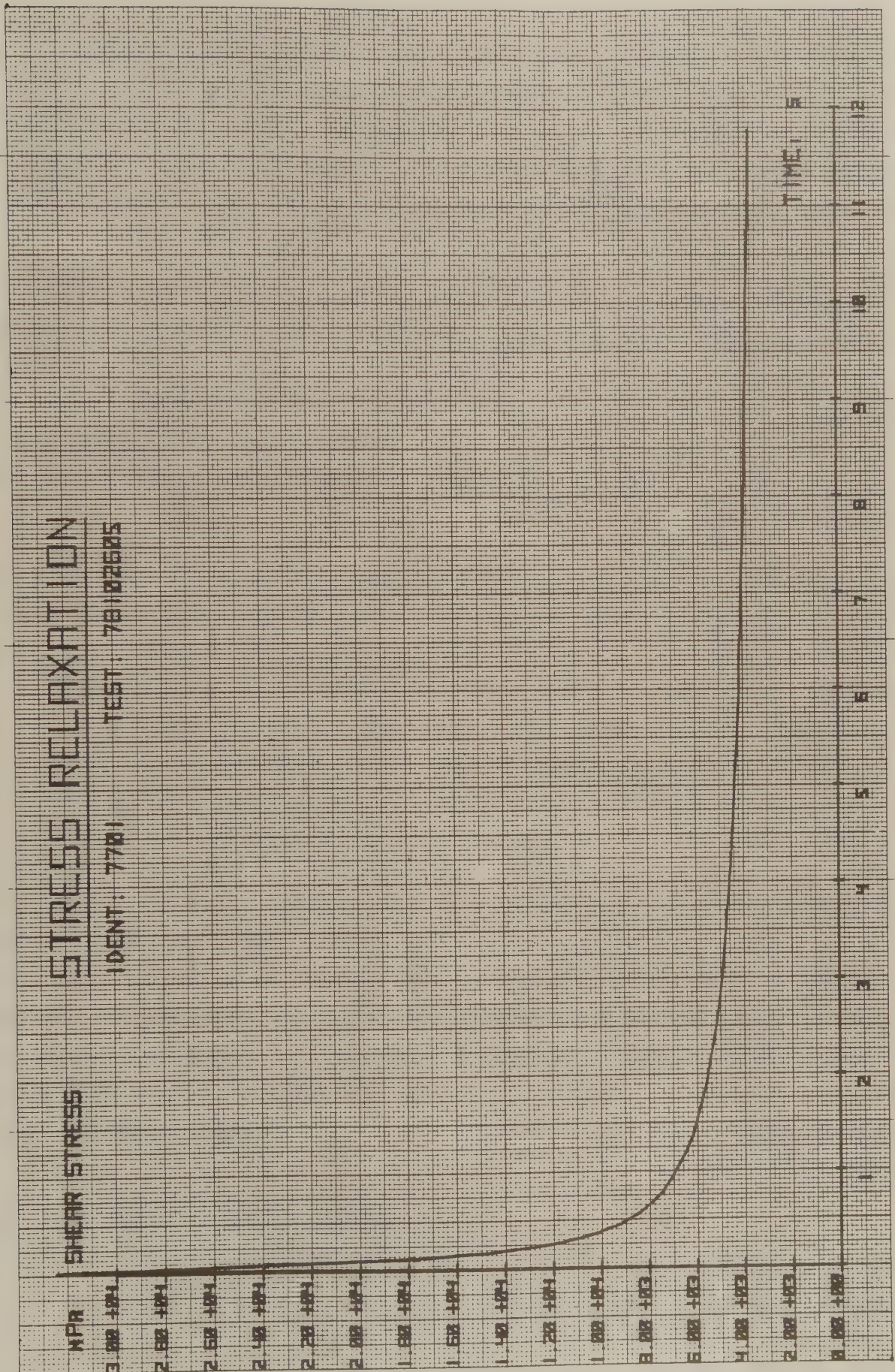


Fig. 3C. Characterization of the rheology prior to application for a flat, white wall paint.

Stress relaxation curve after shearing at 7 s^{-1} and with a cessation of motion within 0.5 s.

The characterization of the changes in the drying period is, therefore, exemplified by a number of alkyd/melamine top coats for kitchen utensiles (D), where practical tests showed different sagging tendencies of the paints. The quality of the various coatings in practical application is characterized by the film thickness range where the various problems did not appear (D).

The measured viscosity during the drying period (figure 4A) reflects the sagging tendency reasonably well (a wrong indication for the film quality of paint 76004 in figure 5 in ref. D should be noted). All the paints showed to be Newtonian in the measurements prior to application, and the differences in sagging tendency, therefore, were to be sought in the drying behavior of the paints.

Comparing the viscosity increase in the drying period (figure 4A) to the evaporation from the paint films (figure 4B) shows only partial accordance. The paint 76005, having the slowest viscosity increase, is found to have a faster evaporation than does the paint 76002. The solvents in these paints are mixtures of 5-6 different solvents and the solvent power and the viscosity of the remaining solvents, therefore, change as the evaporation proceeds. The solvent balance of the different mixtures as the drying proceeds is calculated and in figures 4C and 4D are shown how the solubility parameters and the solvent viscosity, respectively, change as the evaporation proceeds. Here paint 76002 shows an increasing marginality in solvent power relative to the resin and an increasing solvent viscosity, whereas the solvent mixture of paint 76005 does not change in solubility power and seems to decrease in solvent viscosity as the evaporation proceeds. Both those effects support a faster viscosity increase in paint 76002 compared to 76005.

The capability of the characterization to reflect leveling/sagging qualities of coatings in practice is demonstrated in a number of cases (C, D, G).

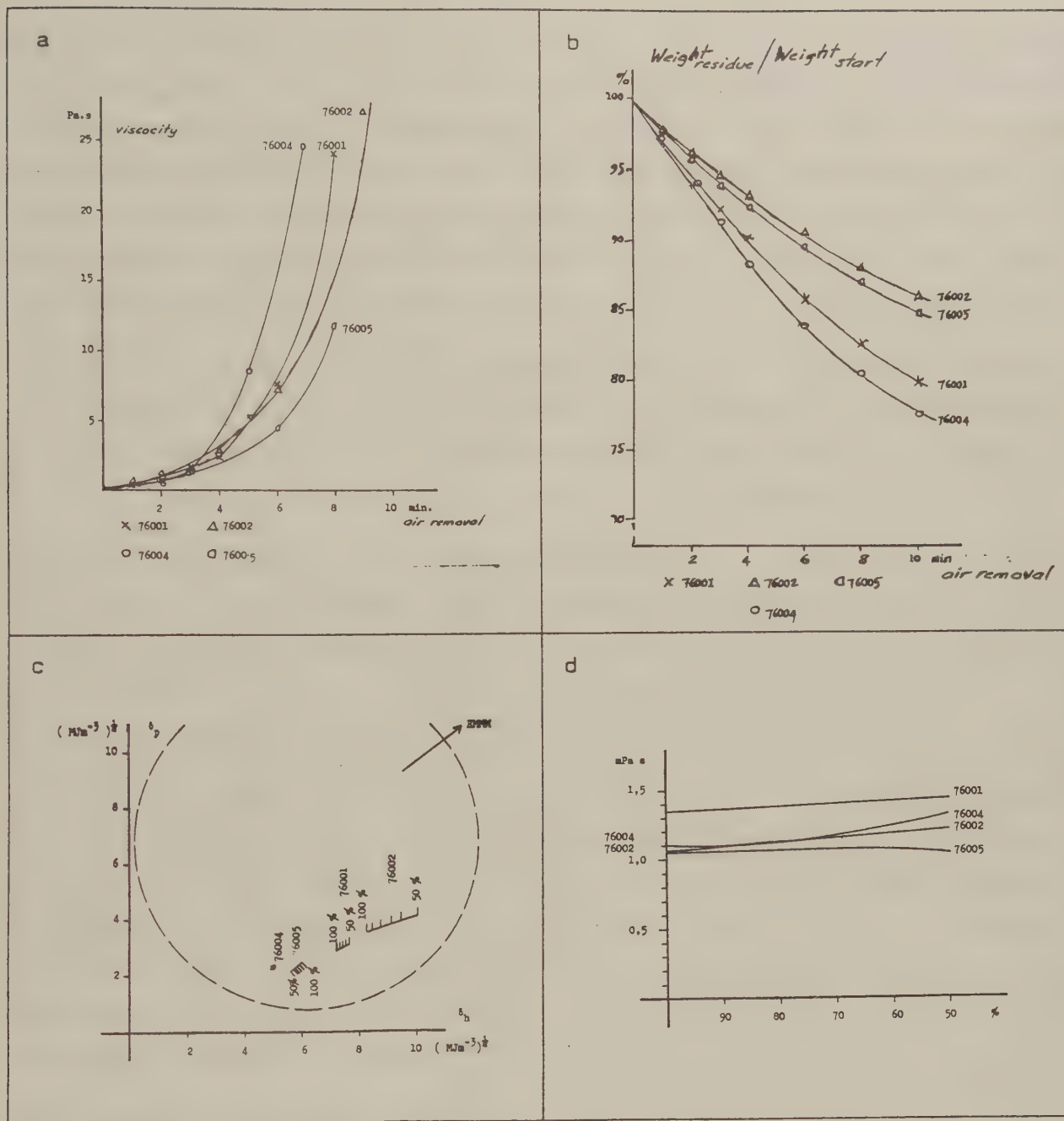


Fig. 4. The changes in the drying period in a number of alkyd/melamine top coats for kitchen utensiles.

- The viscosity during drying measured at a shear stress of 25 Pa in films applied by a draw-down bar with 100 μm gap-size.
- Evaporation in the drying period for paint films applied as in the viscosity measurement.
- Solubility parameters of the solvent mixtures as the drying proceeds. The change in mixture during drying is calculated from evaporation rates of the pure solvents. The percentages in the figure express the remaining amount of solvent relative to the initial amount. The solubility area for a polyester is also indicated. The arrow indicates how the solubility area will change with addition of melamine.
- Viscosity of the solvent mixtures as the drying proceeds.

In one case the measurement of viscosity during drying for a shear thinning paint indicated an unrealistic low viscosity profile compared to the ranking of sagging tendency relative to two similar but Newtonian paints (G). This divergence is due to the shear stress of 25 Pa in the measurement, which leads to a relatively lower measured viscosity for the shear thinning paint compared to the viscosity at 1 Pa, which is the stress typical for sagging.

A smaller stress in the measurement, e.g. 10 Pa would still be reasonable with respect to leveling and is, therefore, only a problem of having a sufficient accuracy in a measurement with a lower shear stress.

Another limitation in the characterization is found in the evaluation of the viscosity increase due to evaporation for coatings containing thickening agents. In an investigation of the impact of thickening agents (G) it was found that even though the presence of a thickening agent did not change the initial properties of the coating, the viscosity increase in the drying period was accelerated compared to the paint without thickening agent. This means that the influence of the thickening agent may increase as the concentration of volatiles decreases. The viscosity increase with evaporation, therefore, cannot be fully evaluated from volatile/resin considerations alone. This may also explain why the paint 76003 in ref. D did not have a viscosity increase in accordance with evaporative behavior, since this group of paints contained different amounts of thickening agents.

The evaluation of the volatile balance, and subsequently of viscosity, in the drying period assumes a certain degree of ideality in the interaction between volatiles and polymers, which is not present in "solubilized" water-dilutable coatings (F, G). This problem will be discussed in detail in the next chapter.

In airless spraying of a number of paints (D) no connection was found between the rheological characterization and the tendency of the paints to develop craters. Strong indications were found for the craters to be caused by the impact of the spray drops on

the paint film. The cratering should, therefore, be related to the atomization of the paints. The atomization in airless spraying follows from the edge of a spray sheet formed in front of the nozzle (56). This spray sheet is formed by a two-dimensional elongation and the formation of sheet and subsequently drops is a matter of very short time (milliseconds). Both elongational viscosity and elasticity must, therefore, be expected to be involved in the atomization. The measurement of elongational viscosity is not included in the characterization and methods of evaluation of elongational viscosities remain to be developed for low viscosities as in coatings. The elasticity measurement in the characterization remains to be tested against this problem.

In the situations where surface properties, different from those of the bulk film, are present, the rheological characterization is not alone capable of describing the in practice observed behavior. An example on this is the release of air bubbles in different automotive coating films (C). The presence of blisters due to boiling can only be related to the characterization to the extent it is related to the remaining amount of volatiles in the film at the time of temperature elevation. In the different problems of craters and bubbles the bulk rheology is only one of a number of parameters, as discussed in chapter 2.

The applicability of generalized Newtonian, linear and quasilinear viscoelastic models is exemplified in figure 5 on a Saran solution.

Numerically the models give the following results for the Saran solution:

Model	Relations closest to data	Correlation coefficient
Newton	$\tau = 764 \text{ mPa s} \cdot \dot{\gamma}$	0.948
Bingham	$\tau = 62500 \text{ mPa} + 695 \text{ mPa s} \cdot \dot{\gamma}$	0.958
Power Law	$\tau = 8170 \text{ mPa s} \cdot \dot{\gamma}^{0.66} [\text{s}^{-1}]$	0.986
Casson	$\eta^{\frac{1}{2}} = (1435 \text{ mPa s})^{\frac{1}{2}} + (2435 \text{ mPa}/\dot{\gamma})^{\frac{1}{2}}$	0.868
Carreau	$\eta = 146 \text{ mPa s} + 15955 \text{ mPa s} [1 + (6.9 \dot{\gamma})^2]^{\frac{0.65 - 1}{2}} [\text{s}^{-1}]$	curve-fitting

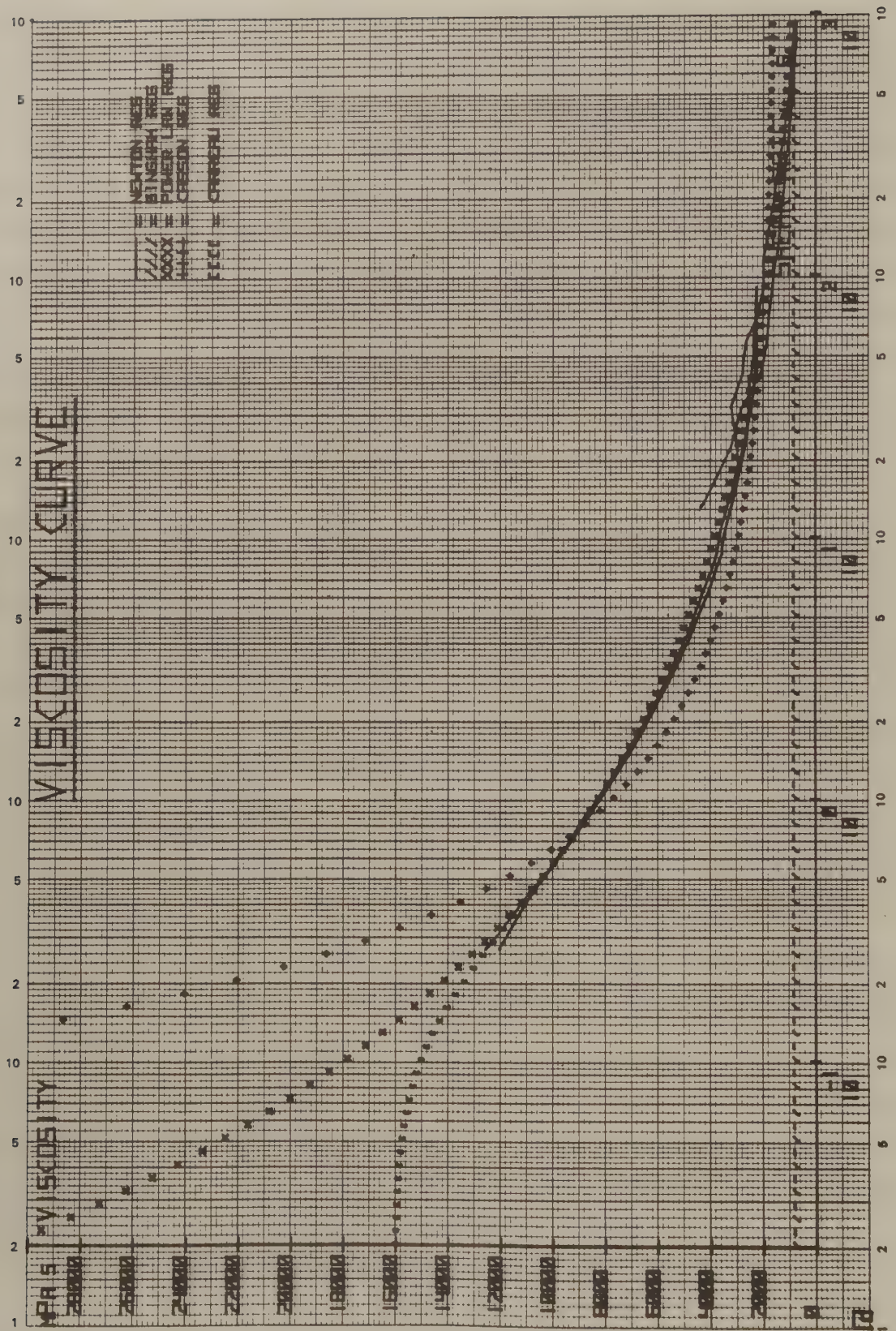


Fig. 5. The viscosity curve for a Saran solution approximated by different rheological models. The coefficients of the indicated closest approximations are indicated in the text.

The application of these relatively simple models on one material shows the possibility of comparing different materials by numerical values from reasonable models either generally or in limited ranges. It also shows the capability of describing a material from limited data when the nature of the material is known. The example, furthermore, illustrates the limitations in applying a model to a material uncritically and extrapolating uncritically.

The practical usefulness of such models applied directly on the measured data is illustrated in figure 6, where three thixotropic alkyd resin variations are compared as a product control. All three products were fitted very well by a power law expression in the shear rate measurement from lower than 0.1 s^{-1} and up to 10.000 s^{-1} . The regression results are shown in figure 6A. The measured data have been shown by measurement intervals as each material has been measured with three different geometries. In figure 6B and 6C the thixotropic recovery and stress relaxation, respectively, are fitted to models of an exponential type (Maxwell, see ref. D), which all are seen to be very good fits. The numerical expressions in the models for the three resins are the following:

Resin	Shear rate relationship Power Law	Thixotropic recovery
1	$\tau(\dot{\gamma}) = 6077 \dot{\gamma}^{0.55}$	$\tau(t, 700 \text{ s}^{-1}, 0.7 \text{ s}^{-1}) = 197 \text{ mPa} - 6459 \text{ mPa} \cdot e^{-\frac{t}{162\text{s}}}$
2	$\tau(\dot{\gamma}) = 2662 \dot{\gamma}^{0.61}$	$\tau(t, 700 \text{ s}^{-1}, 0.7 \text{ s}^{-1}) = 135 \text{ mPa} - 4021 \text{ mPa} \cdot e^{-\frac{t}{108\text{s}}}$
3	$\tau(\dot{\gamma}) = 43050 \dot{\gamma}^{0.33}$	$\tau(t, 700 \text{ s}^{-1}, 0.7 \text{ s}^{-1}) = 329 \text{ mPa} - 25806 \text{ mPa} \cdot e^{-\frac{t}{31\text{s}}}$

Resin	Stress relaxation
1	$\tau(t, 7 \text{ s}^{-1}, 0 \text{ s}^{-1}) = 1167 \text{ mPa} + 3595 \text{ mPa} \cdot e^{-\frac{t}{1.07\text{s}}}$
2	$\tau(t, 7 \text{ s}^{-1}, 0 \text{ s}^{-1}) = 546 \text{ mPa} + 2486 \text{ mPa} \cdot e^{-\frac{t}{0.94\text{s}}}$
3	$\tau(t, 7 \text{ s}^{-1}, 0 \text{ s}^{-1}) = 5887 \text{ mPa} + 26921 \text{ mPa} \cdot e^{-\frac{t}{0.88\text{s}}}$

Power law approximation of the shear rate dependency being a good description of the viscosity up to 10.000 s^{-1} .

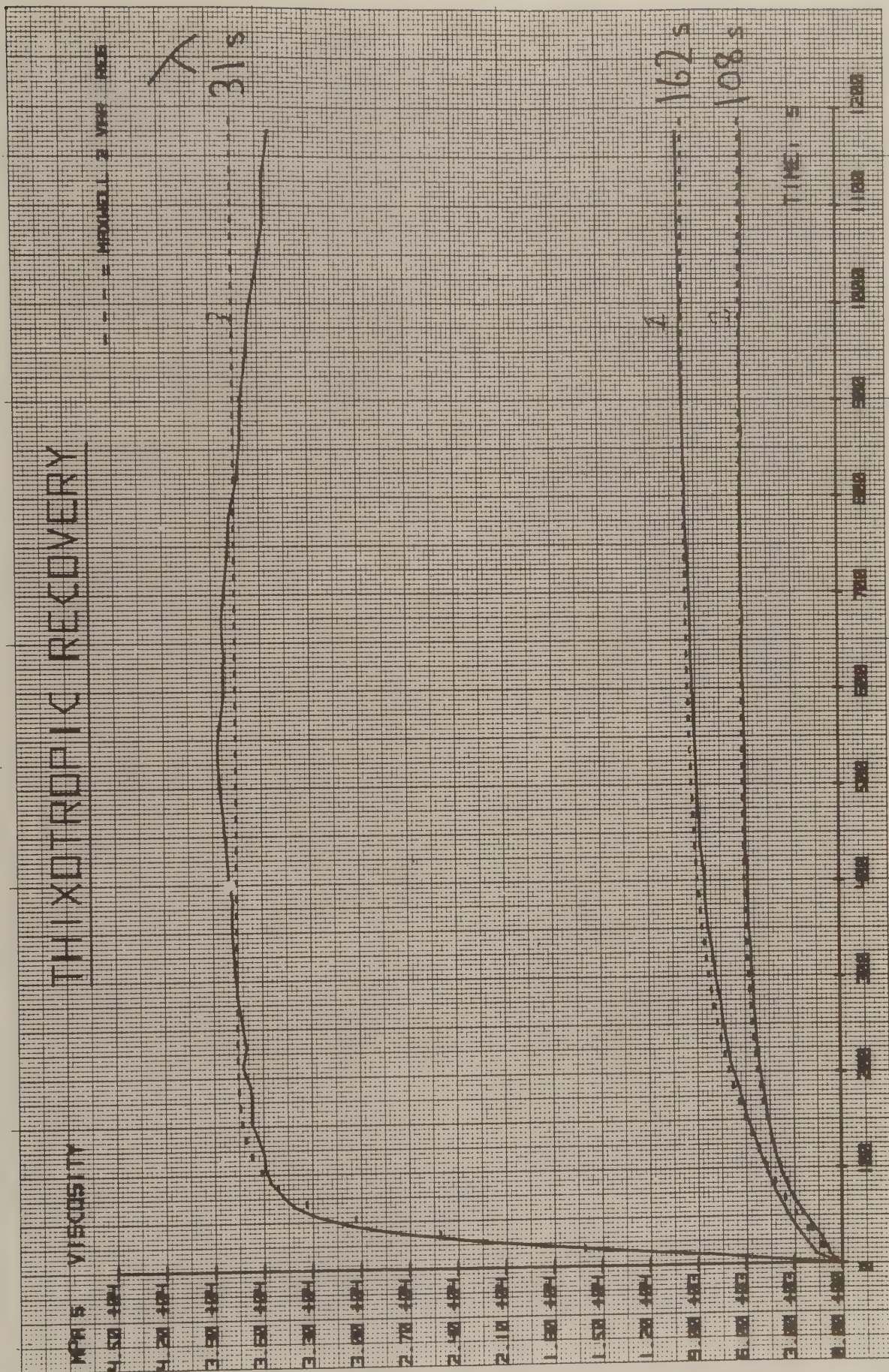


Fig. 6B. Approximation of the rheological properties for three thixotropic alkyd resins by rheological models. The coefficients of the approximations are given in the text.

Exponential recovery of viscosity at 0.7 s^{-1} after shearing at 698 s^{-1} .

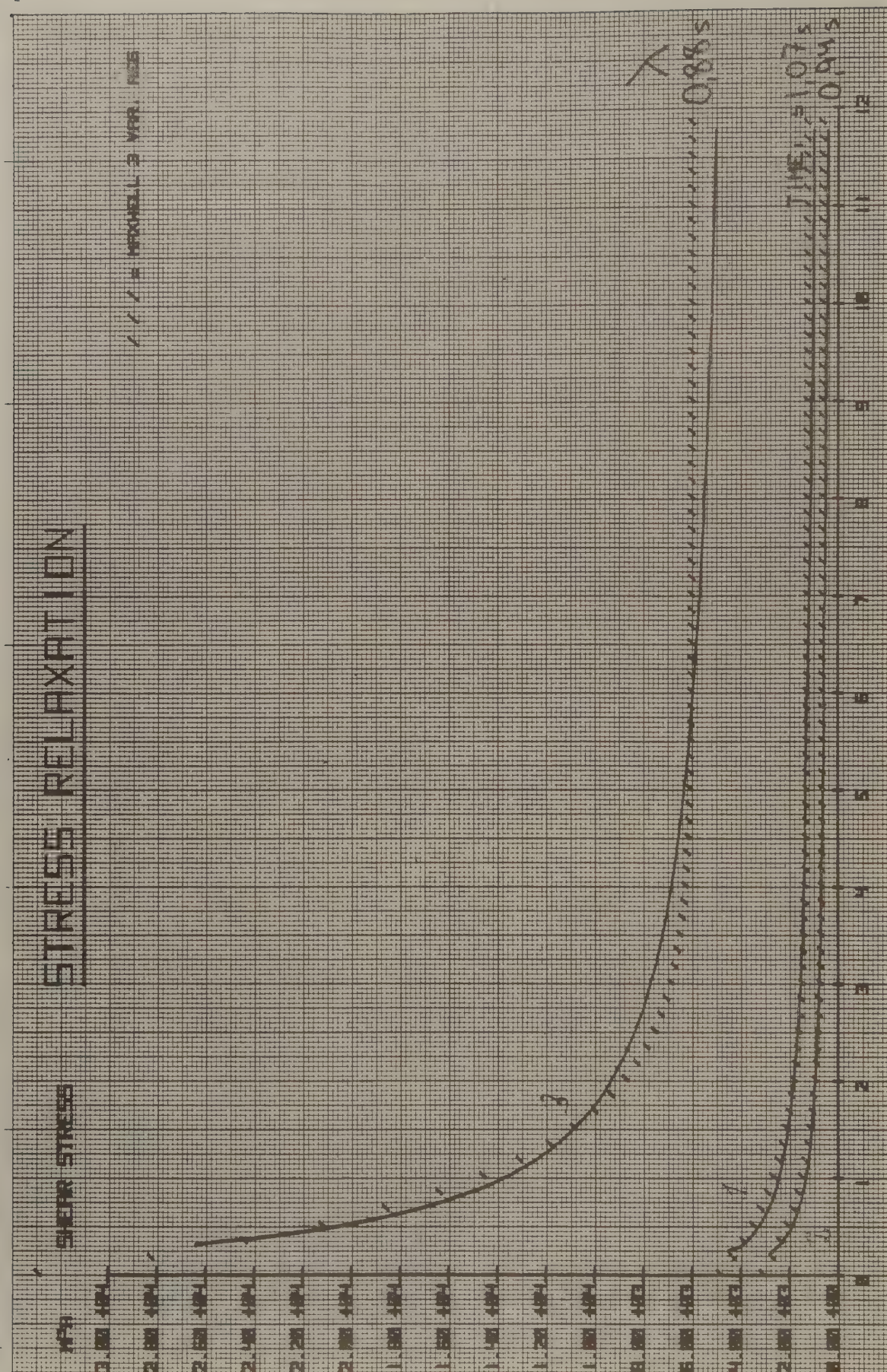


Fig. 6C. Approximation of the rheological properties for three thixotropic alkyd resins by rheological models. The coefficients of the approximations are given in the text.

Exponential stress decay to a finite value after shearing at 0.7 s^{-1} and cessation of motion in less than 0.5 s .

The numerical coefficients are seen to be capable of reflecting the differences in shear thinning (the power law exponent), thixotropy (a relaxation time), elasticity (a relaxation time) as well as plasticity (the yield stress in the relaxation measurement). Furthermore, the degree of shear thinning and thixotropy are seen not to be related.

A more interesting result from this measurement is maybe that the relaxation times in the elasticity and thixotropy measurement differ two orders of magnitude (of order 1 and 100 s, respectively), thus supporting the idea of having a first approximation of the entire flow behavior of the material being a viscoelastic model of three relaxation elements (6 relaxation times). In the considered models the shear rates in the transient measurements are not expressed explicitly and are, therefore, included in the relaxation times. The relation between the two relaxation times may thus be altered when made independent of shear rate. A general model of this type may be solved for the three measurement flows (41). If such a model gives reasonable agreement for a material in such three different measurements, it may be used to evaluate the flow behavior of the material in other flow situations, e.g. the two-dimensional elongational flow in airless spraying. The solution of the general equation for elongational flow seems to be more complicated than for the shear flows.

4. Evaporation from Aqueous Systems (F, G)

The rheology of coating materials is purely a mechanical description and the validity of the rheological characterization, therefore, is independent of the composition and drying processes of the coating.

The evaluation of the drying behavior following the evaporation, however, is closely related to the evaporative and chemical characteristics of the constituents of the coating. The techniques of evaluating the evaporative behavior and its impact on viscosity discussed in the preceding assume that the coating can be considered as a solution of a polymer in moderate concentration in organic solvents. These evaluation techniques, therefore, are not necessarily valid for the newer, environmentally more favourable coating types, as water-dilutable coatings.

The means of describing the evaporative behavior when water is one of the volatiles is discussed in the following.

4.1 Evaporation of Water

The evaporative behavior of mixtures of organic volatiles may be described sufficiently accurate from a technological point of view by isothermal mass transfer from the fluid mixture into surroundings with no content of volatiles. In order to supply evaporative data for the single volatiles independent of measurement conditions, these are usually given in terms of evaporation rates relative to a reference volatile (usually n-Butylacetate or Ether). The non-ideal interaction among the volatiles in the mixture may also be taken into account in a practicable way (57).

When water is considered as one of the volatiles this description is not readily applicable, since the physical properties are numerically quite different from those of the organic volatiles and since there will always be a concentration of water in the surroundings.

Assuming isothermal conditions it may be shown that the evaporation rate of water varies linearly with the concentration of water vapor or the relative humidity in the surroundings. This will also apply to an evaporation rate relative to any reference volatile with an evaporation rate independent of the humidity. This relationship is verified experimentally as shown in figure 7 which also gives the relative evaporation rate values for water relative to n-Butylacetate as:

$$\text{RER} = 80 \left(1 - \frac{\text{RH}}{100}\right)$$

The evaporation of water is found to be more sensitive to the heat transfer situation than moderately fast evaporating organic solvents. The evaporation rate varies generally with the square root of the air velocity, when forced convection dominates the free convection. Forced convection increasing the evaporation rate may lead to lower surface temperatures for water and for fast evaporating organic solvents, when the heat transfer from the interior of the film substrate becomes insufficient. This may limit the impact of air velocity on the evaporation rate.

4.2 Evaporation of Mixtures of Volatiles Containing Water

When water is one of the volatiles in a mixture, information on the non-ideal interaction between water and the organic volatiles is not readily available. The volatile balance has, however, been applied to mixtures of volatiles containing water assuming ideal behavior. In the majority of cases this has shown to be sufficiently accurate even quantitatively assuming a reasonable evaporation rate for water in the situation considered. Applying the linear humidity dependent evaporation rate of water to the evaporation of one mixture at different relative humidities (figure 8A) shows that this description is capable also of reflecting the changes in evaporation balance with changes in the relative humidity.

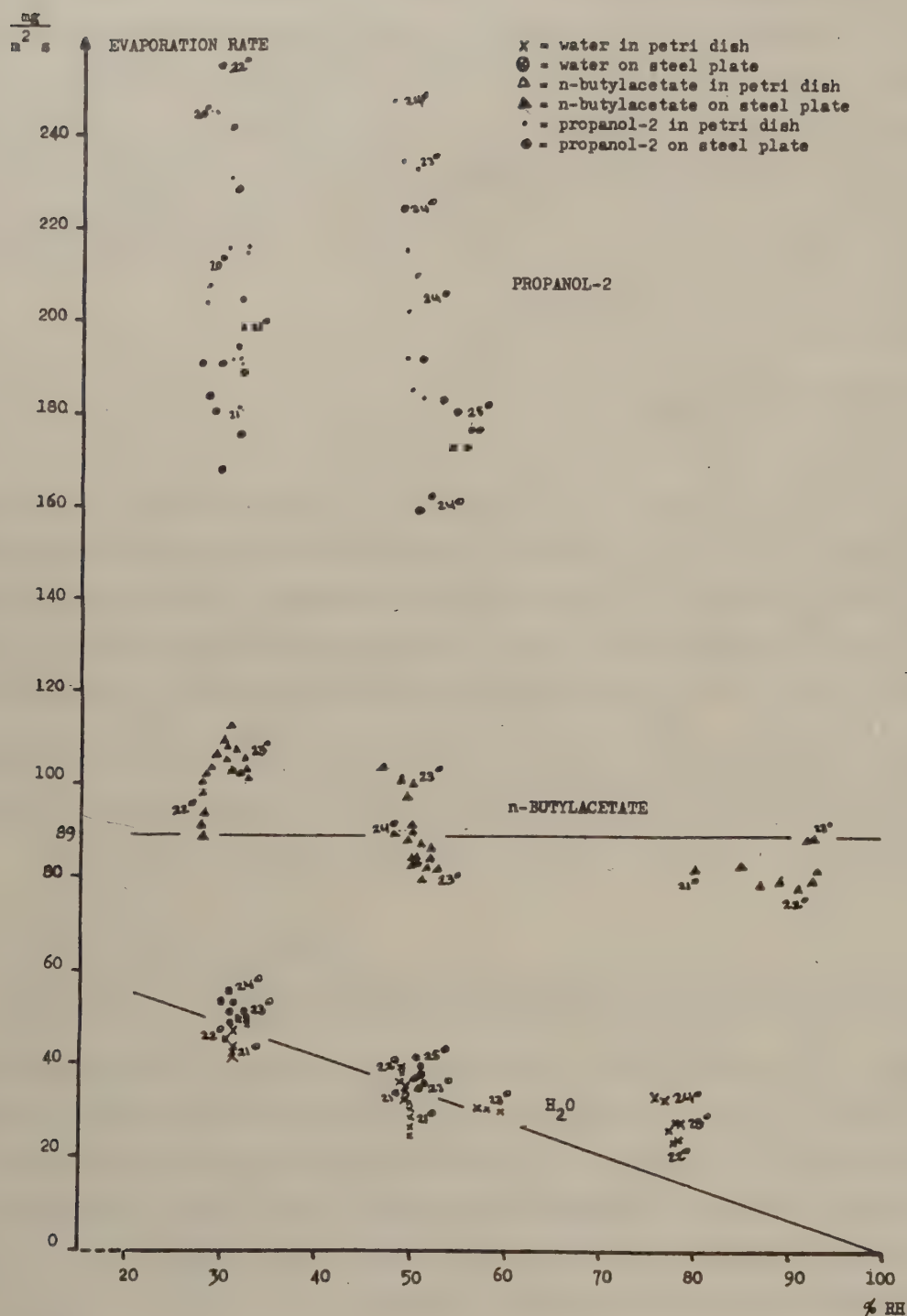


Fig. 7. Absolute evaporation rate for different volatiles as function of relative humidity. The measurements are made in a closed room without forced convection from a 150 • 70 • 2 mm liquid film in an 1 kg steel block and a 20 mm deep 90 mm Ø petri dish. The numbers in the diagram indicate the room temperature during measurement.

The theoretical basis and calculation procedures to calculate activity coefficients for mixtures of volatiles containing water are available (58, 59) as an extension of the thermodynamical considerations on the properties of molecular segments which give the activity coefficients for organic volatiles, and this might be fitted into a practical system as that for organic volatiles.

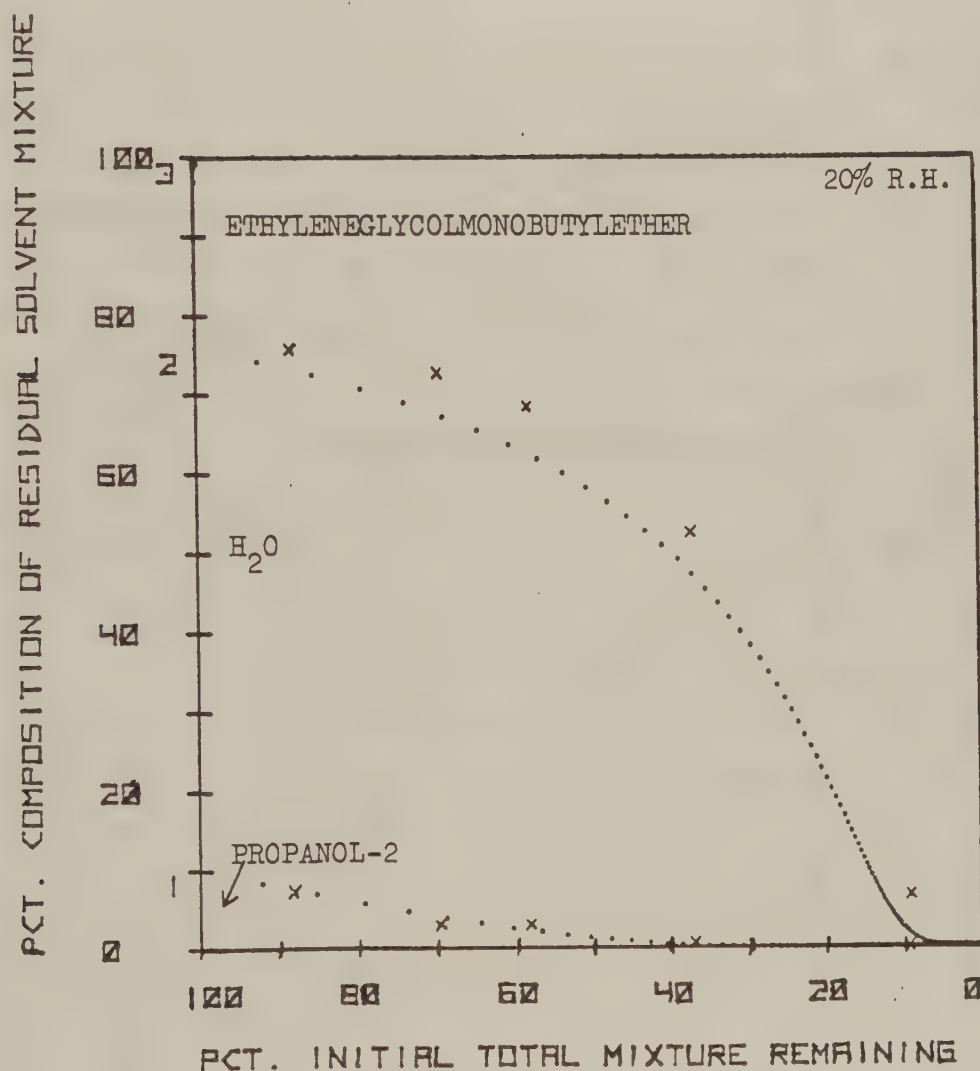


Fig. 8A. Volatile balance of ternary mixture of Propanol-2, Ethyleneglycolmonobutylether and water as the evaporation proceeds at 23°C and 20% R.H. The calculated curve is determined from relative evaporation rates as indicated in figure 7.

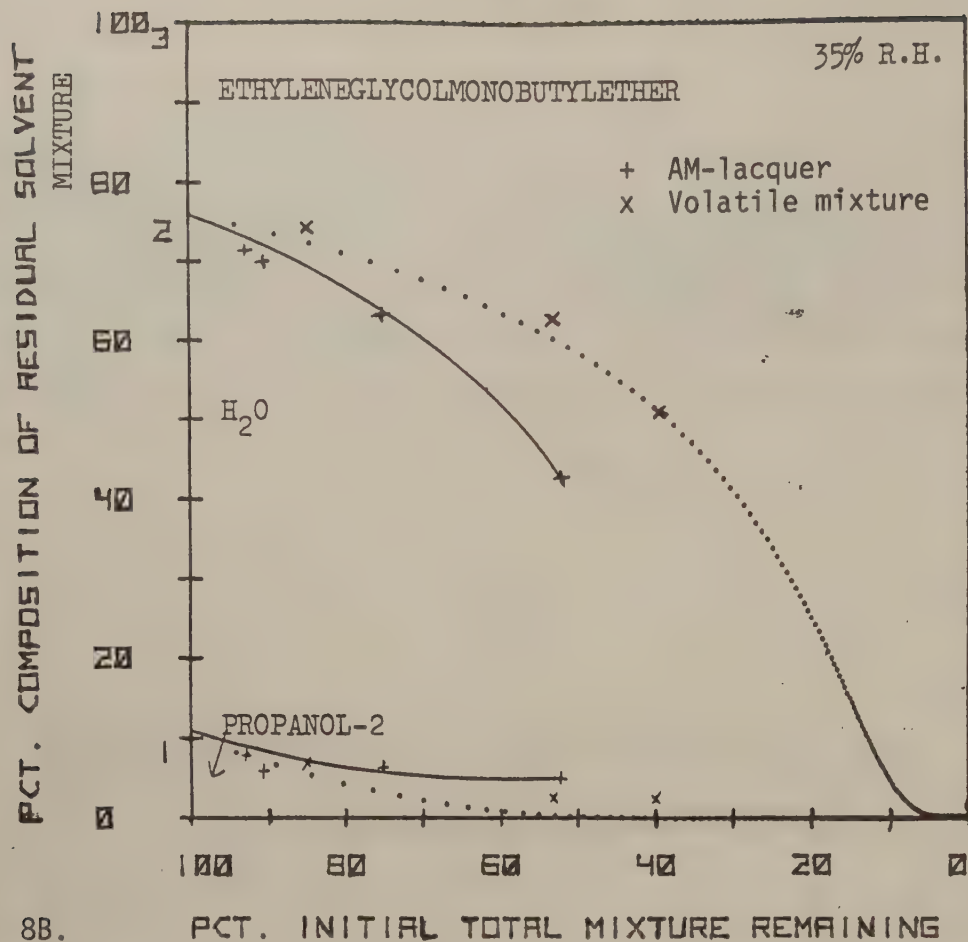


Fig. 8B.

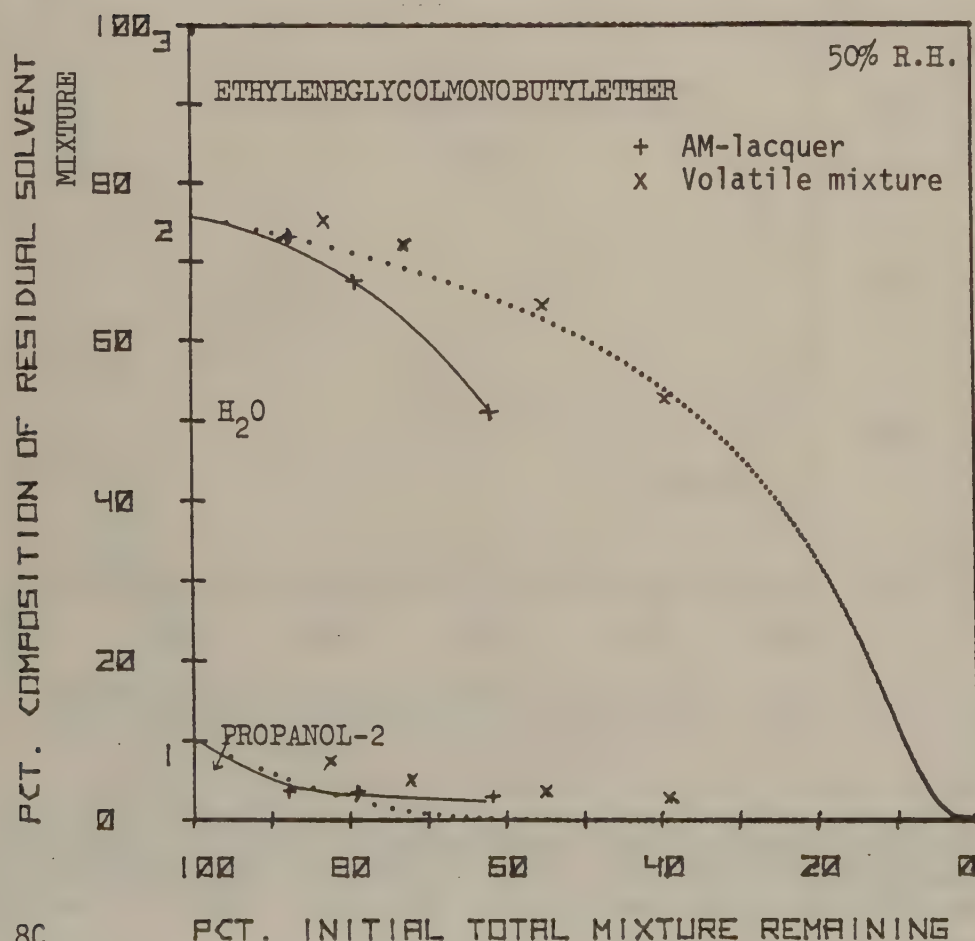


Fig. 8C.

Fig. 8B and C. Predicted and measured volatile balance for the considered mixture of volatiles compared to the balance of the alkyd/melamine lacquer with the same initial volatile composition.

B. Evaporation at 23°C and 35% R.H.

C. Evaporation at 23°C and 50% R.H.

4.3 Evaporation from Solutions and Dispersions

The application of the calculation of the volatile balance on a mixture of volatiles on coating materials with a non-volatile content assumes that the non-volatiles do not interact non-ideally with the different volatiles. This is a good approximation to solution systems of a not too high solid content. Water-dilutable coatings are either based on emulsions or marginally water soluble polymers.

In case of emulsions the continuous phase is almost exclusively water and the fluid period of the drying may thus be regarded as evaporation from a water film containing particles. If the evaporation of organic volatiles should be taken into account in this period, the evaporation of the organic volatiles could be regarded as a two-step mass transfer: From emulsion drops to the continuous phase to the atmosphere.

The polymers for water-dilutable coatings are not fully soluble in water because of the required water resistance of the dry film. The resins to be solved in mainly water are usually made compatible with water by hydroxylic and amine-neutralized carboxylic groups and an addition of a certain content of organic volatiles. Applying the calculation of the evaporation of a mixture of volatiles to systems of this type need not give a true picture of the evaporation behavior as shown in figures 8B and 8C, where an alkyd/melamine lacquer (3:1 oilfree polyester based on adipic acid, isophthalic acid, neopentylglycol, and trimethylpropane) neutralized to pH 8 by Dimethylaminoethanol is considered. A much faster decrease in the relative content of water is observed than indicated by the calculation.

Observing the alkyd/melamine lacquer visually it is found to be slightly hazy until approximately 25% of the volatiles have evaporated. This indicates the presence of several phases in the film. In a two-phase system the concentration of volatiles in the continuous phase may differ from the total if the individual volatile

components have different affinities for the discontinuous phase. This has been shown to be true (60, 61) with organic volatiles tending to concentrate in the organic (polymer) phase in emulsion systems. This seems to cause the relatively faster evaporation of water than expected when the resin is present. Since this is not the case when the same volatile mixture is regarded alone (figure 8) it indicates that the polymers should be included in the evaluation of non-ideal molecular interaction when water-dilutable coatings are considered. This should be possible in the theories and techniques of Prausnitz and Fredenslund et al. (58, 62).

The evaporation from this type of material may also be approached from an emulsion point of view with a two-step mass transfer. Even though the polymer is very heterogeneous it does not lead to a simple emulsified system because of the size and complexity of the polymer molecule, but it is known to form different structures in the concentration range of application and drying of coatings. When the water content is decreased the coatings seem to change from being emulsion-like in water at the application concentration to be a very unordered structure and finally become solution-like in organic solvent. This is seen very strongly on the changes in viscosity, where decreasing water content leads to a sudden viscosity increase followed by a stagnation in viscosity, either following a viscosity maximum or just as a plateau, and finally a monotoneous viscosity increase.

It seems that the viscosity anomalies, and thus the structure, diminish with better solubility of the polymer in the volatile mixture. This means an increase in the amount of hydroxylic and carboxylic groups on the polymer, an increased extent of neutralization or larger amounts or solubility power of organic volatiles (G).

This last point in turn shows that the water/organic volatile balance as the drying proceeds directly affects the extent of structure formation and thus the development in viscosity. The viscosity has been compared for the alkyd/melamine lacquer being diluted to application composition with 1) water and with 2) water/

Propanol-2 and finally 3) the coating as the drying proceeds at 23°C and 50% R.H. Those three composition changes are indicated in phase diagram in figure 9A and the viscosities are shown as function of solid content in figure 9B. This shows the typical viscosity plateau in the range 30-60% solid content when diluted with water as the structure formation with increasing water content opposes the viscosity decrease due to dilution. This effect is less prominent by dilution with the mixture water/Propanol-2.

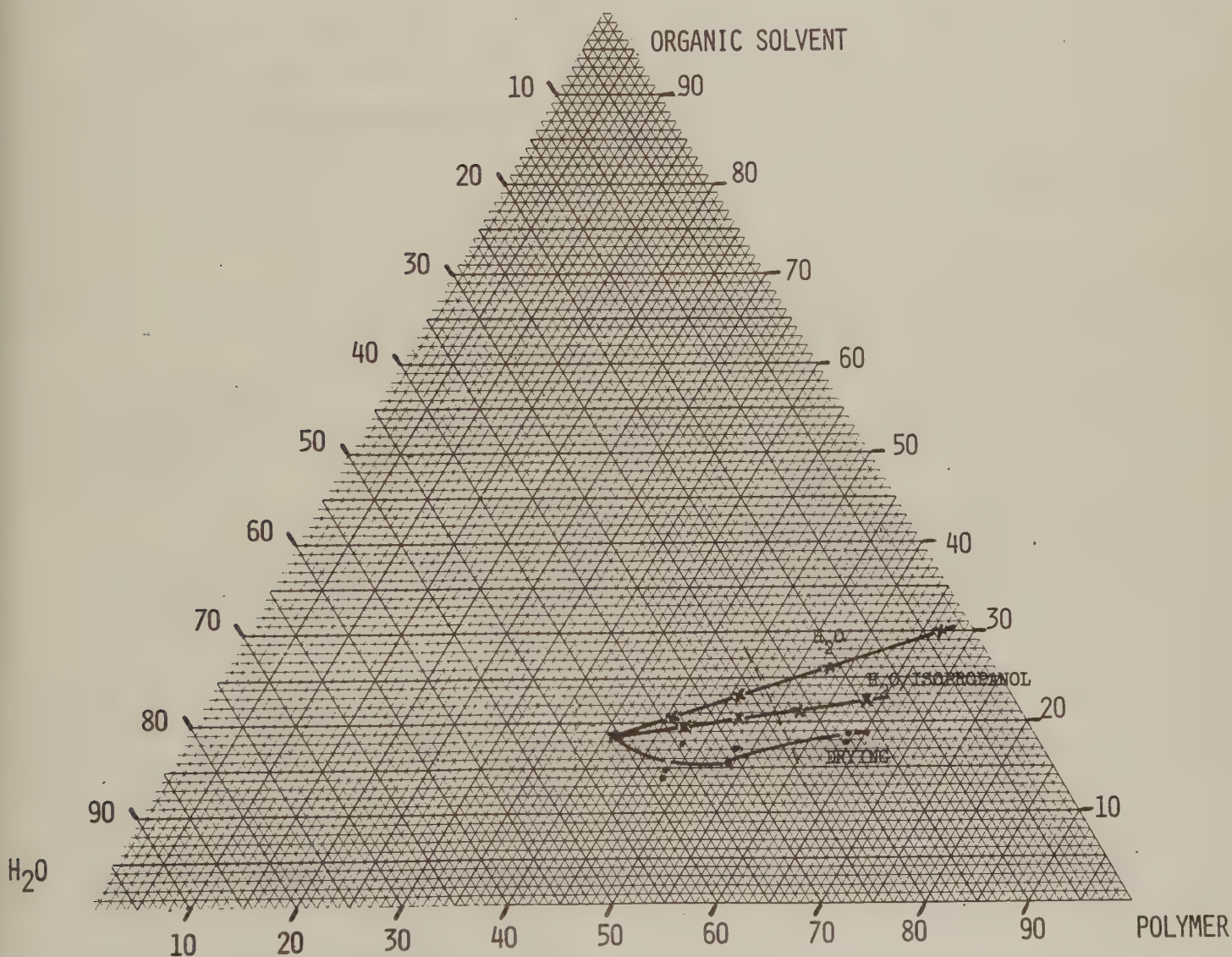


Fig. 9A. The alkyd/melamine lacquer. Polymer/organic volatile/water balance by dilution with water and dilution with water/Propanol-2 (7.4:1 by weight) and by evaporation at 23°C and 50% R.H.

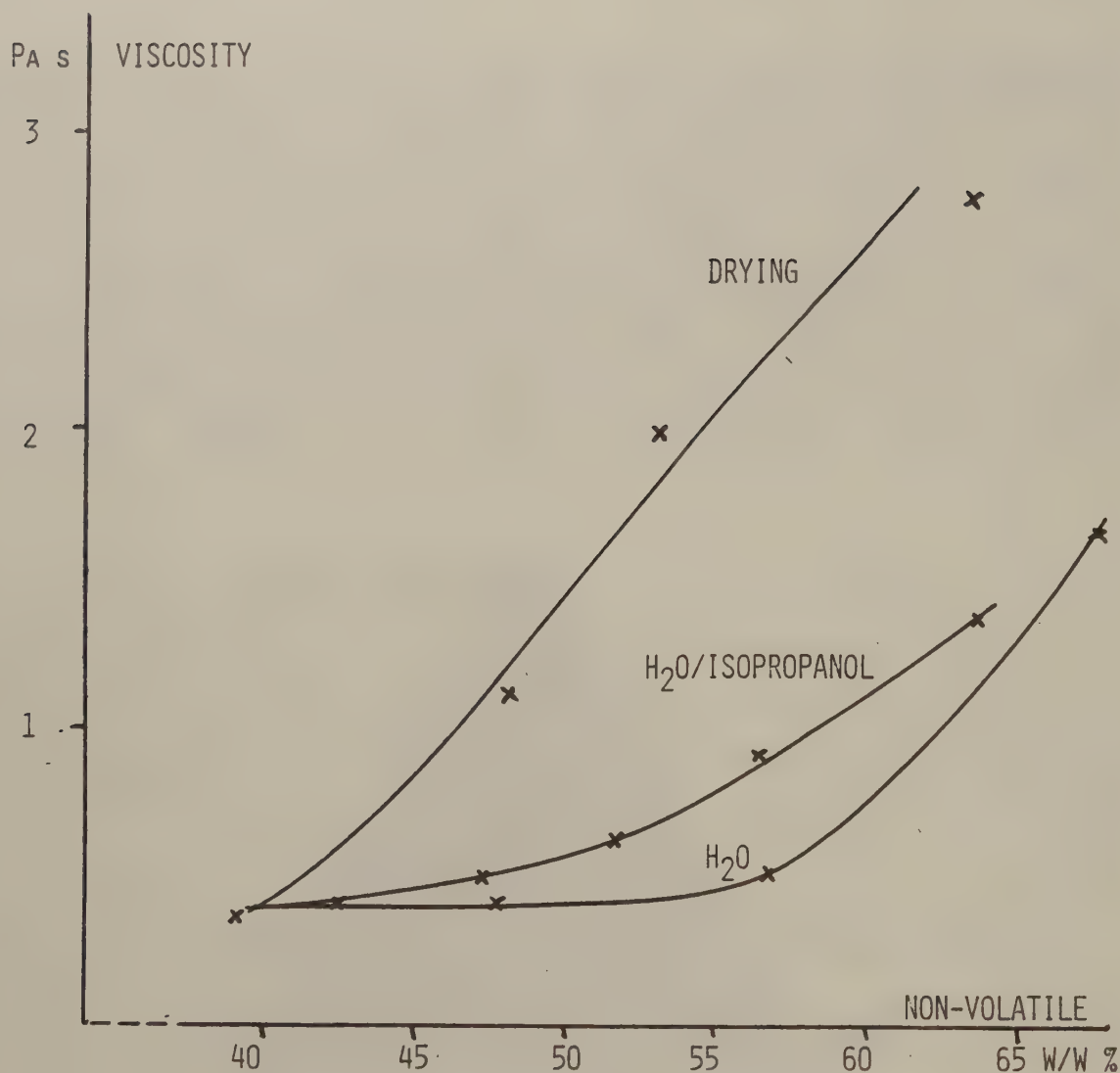


Fig. 9B. The alkyd/melamine lacquer.
The viscosity as function of solid content by those three concentration changes. The lacquer was Newtonian in all measurements.

This is noteworthy since the content of organic volatiles is higher in the system being diluted purely with water. In the case of drying a steady viscosity increase almost as for a true solution is obtained. This indicates that the coating system possesses different liquid structures depending on the balance between polymer/organic volatile/water equivalent to the behavior of more well-defined surface active materials. The considered polymer is much larger and more complicated than surfactants and the structures in this system cannot be expected to be well ordered as do surf-

actant systems. In figure 9A is indicated where the coating becomes visually fully transparent as the content of water becomes below approx. 24%.

When analyzing the viscosity of this alkyd/melamine coating system on a solubility parameter basis it seems that the relative viscosity increases as the solubility parameters become more marginal to the unneutralized alkyd as indicated in figure 10A and 10B. The data presented in figure 10 are on the alkyd/melamine coating in different volatile mixtures but with the same non-volatile content. The measurements of Magdanz (63), also covering a concentration range, indicate too that the relative viscosity is increased by a stronger hydrogen and weaker polar bonding. This finding indicates that the content and solubility power of the organic volatile effect the backbone of the polymer, and thus the viscosity, in the same way as for true solutions whereas the hydrophilic end groups are not affected.

The solubility parameter concept describes the secondary bondings for molecular units and can, therefore, not be expected to be capable of describing the special behavior of the different molecule segments, which cause the structure formation. The solubility parameter concept is based on the same thermodynamic theories as is the description of the molecular interaction in evaporative behavior, and the solubility parameter concept could, therefore, be extended to take the single molecular groups into consideration in the same way as the non-ideal molecular interaction in the description of evaporation. This approach has been taken for a few surfactants (64) and also for a polyester (65).

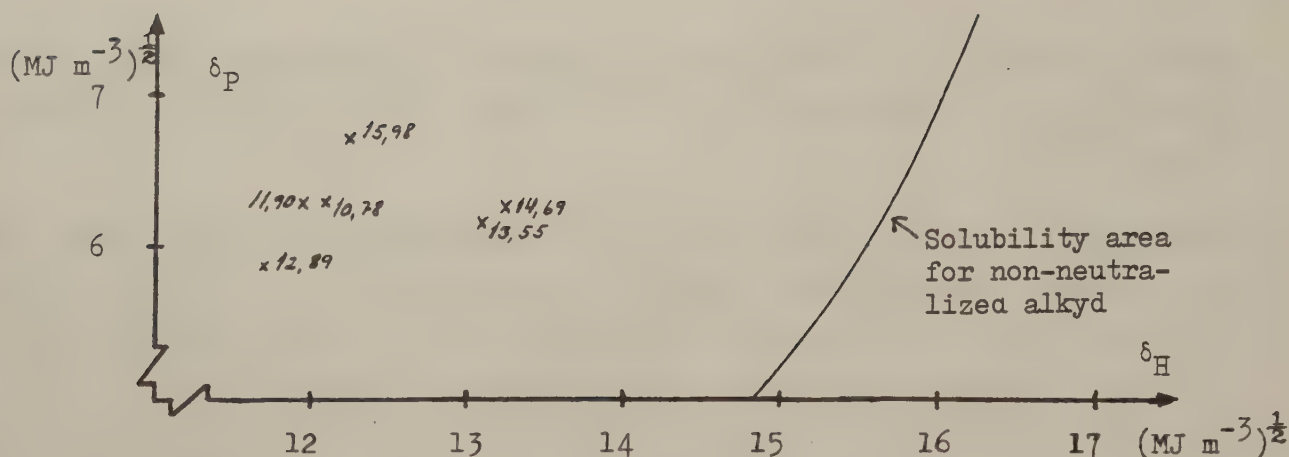


Fig. 10A. Solubility parameters for the different volatile mixtures in the alkyd/melamine lacquer and their viscosity relative to the mixtures. The numbers indicate the name and the relative viscosity of the respective lacquer.

The volatile mixture is regarded only as the organic solvents. Both the solid content and the content of organic volatiles are constant.

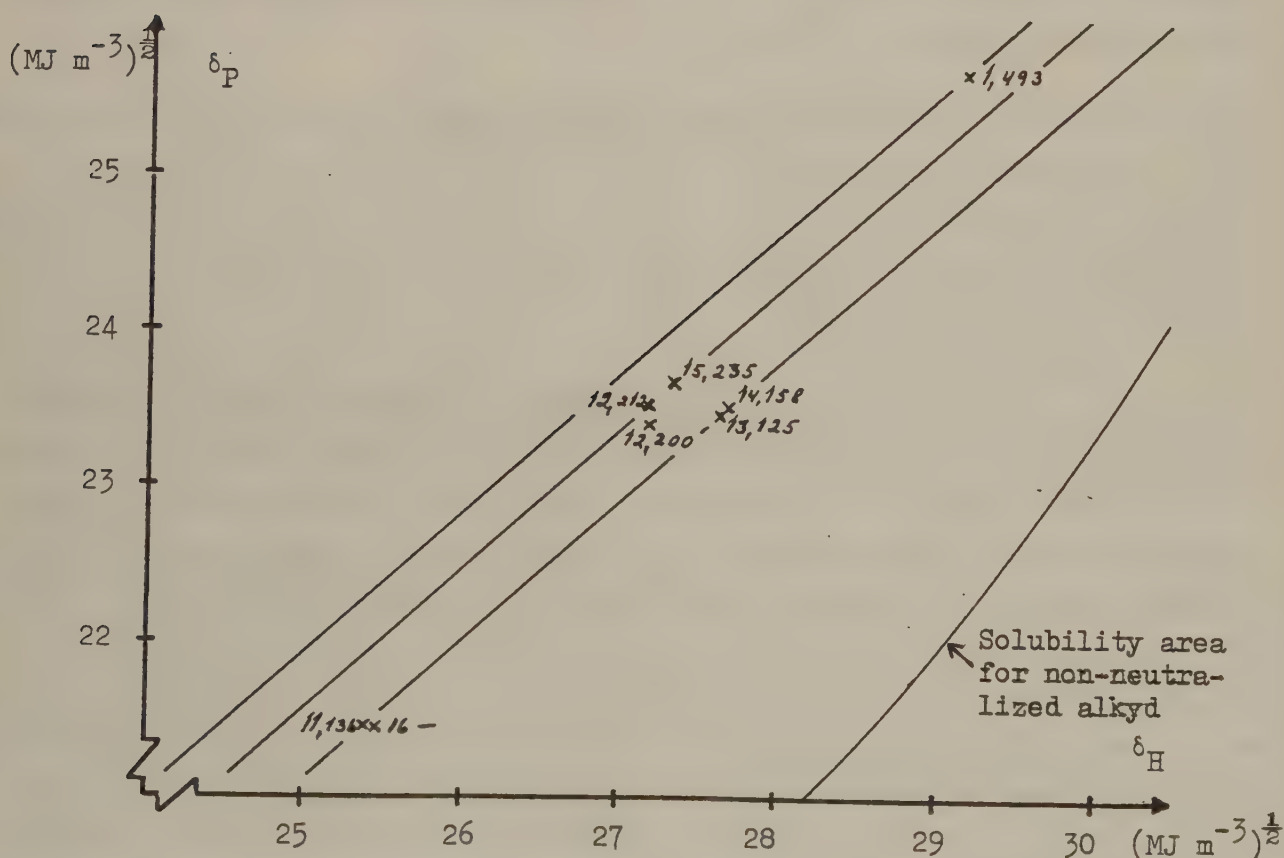


Fig. 10B. Solubility parameters for the different volatile mixtures in the alkyd/melamine lacquer and their viscosity relative to the mixtures. The numbers indicate the name and the relative viscosity of the respective lacquer.

The volatile mixture regarded as water and organic volatiles. The solid content is constant.

5. Conclusion

This study shows that it is possible to characterize the bulk rheological properties of coatings with regard to the application process in a practicable way and in accordance with general rheological theory. It is, furthermore, shown how different rheological models may be applied to the measured data as means of reducing the data and to evaluate flow behavior outside the measured ranges.

In specific application methods elasticity and/or elongational viscosity may be determining for the flow behavior. The validity of the proposed characterization of the elastic properties remains to be tested in detail. In the continued project on airless spraying it is intended to study the atomization and spray mist, but in this process also elongation is expected to be involved. The elasticity measurement should, therefore, also be compared to other types of elasticity measurements. The elongational viscosities of coatings cannot be measured at the present technical level because of the relatively low viscosity. An approach to evaluate elongational viscosity from the three different shear measurements by means of the rheological model has been indicated. This should enable an evaluation of the atomization in airless spraying, and thus the subsequent film quality, from all the different rheological parameters expected to be involved.

The characterization of the viscosity change in the applied film due to evaporation by 1) the loss of volatiles and 2) calculation of solubility parameters of the volatile mixture relative to the solubility region of the resin and 3) calculation of the viscosity of the volatile mixture from the change in volatile mixture as the evaporation proceeds, are seen to be able to reflect the viscosity change in coating systems with normal solid content and a truly soluble resin. In the case of presence of thickening agents the interaction between this and the changing volatile mixture should also be taken into consideration.

When applying this analysis to "solubilized" water-dilutable coatings the lack of practicable information on the non-ideal interaction between water and organic volatiles is apparent, but ignoring this seems to lead to reasonable results in most cases. In such coating systems the volatile/polymer interaction is strongly non-ideal, influencing both the evaporation balance during evaporation and the viscosity change markedly and evaporation calculations can only be used relative to each other. A project is just to be started at the Scandinavian Institute studying the evaporative behavior of such non-ideal systems, but also the solubility parameter concept should be extended to take the heterogeneity of the polymer into account to be able to evaluate the viscosity changes resulting from the composition changes in the drying.

In the situations where surface properties different from the bulk are involved in the occurrence of flow problems, the characterization of the bulk properties is not alone capable of reflecting the observed behavior. The surface properties being involved in the different flow problems are known qualitatively since it is possible to describe the flow problems in a coherent and consistent way. A study of the quantitative behavior of components with affinity to air/liquid surfaces and means of characterizing their behavior with respect to flow problems is on the normal project programme for the Scandinavian Institute for the two coming years.

The ultimate value of being able to characterize and to evaluate the different properties in relation to the application process is to connect the flow behavior to the composition of the coating system. The considered water-dilutable alkyd/melamine coating, therefore, has also been studied varying the different formulation parameters systematically (G). This investigation indicates how the different rheological parameters are controlled by the properties of the single components and their interaction. There exists a certain amount of general knowledge on the interaction of pigment/polymer/volatile and on how this relates to the rheology of the system. This is especially applicable to solution systems but

may be extended to the environmentally more favourable coating types. The long term project on interaction at the Scandinavian Institute is concentrated on the interaction/viscosity relationship for the time being, as the rheometrical instrumentation has become easily available.

This study only considers the coating during drying in an open atmosphere and a fluid period in a curing at elevated temperatures has, therefore, been omitted. A study of the rheological behavior in the coating film as function also of temperature would be a potential continuation of this project. It might at the same time give information on the influence of evaporative cooling on the coating film.

Both the study strictly on rheology and the considerations of properties and behavior of materials are of a general nature and may thus be applied also to other fields than that of coatings.

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